Reproduced
by the

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA

199911171788

5 76 800

DEVELOPMENT AND EVALUATION OF HIGH-TEMPERATURE
RESISTANT COMPOSITE PLASTIC PLATES

28 February 1961

Prepared under Navy, Bureau of Naval Weapons
Contract NOas 60-6099-c

ASTIA

MAY 15 1961

FINAL REPORT

41- 3- 1
XEROX
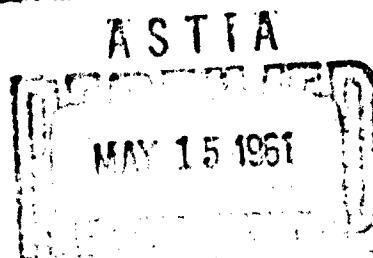
15 December 1959 - 14 February 1961

$7.60

MIDWEST RESEARCH INSTITUTE

DEVELOPMENT AND EVALUATION OF HIGH-TEMPERATURE
RESISTANT COMPOSITE PLASTIC PLATES

28 February 1961

Prepared under Navy, Bureau of Naval Weapons
Contract NOas 60-6099-c

FINAL REPORT

15 December 1959 - 14 February 1961

M.R.I. Project No. 2380-C

Midwest Research Institute
Kansas City, Missouri

ABSTRACT

The tensile and flexural properties were determined for the resin obtained from the diglycidyl ether of bisphenol A and 6.5 pph of trimethoxyboroxine. The resin has high ultimate flexural and tensile strengths (20,810 psi and 13,090 psi, respectively, at 76°F). The strength retention up to 300°F has been determined. About 5 per cent of the 76°F flexural strength is retained at 300°F. This cured resin should be usable in three-layer canopies at skin temperatures up to 350°F.

Maximum thermal rigidity was obtained from the hexahydrophthalic anhydride - vinylcyclohexene dioxide resins at a ratio of 0.7 to 0.8 mol anhydride per mol equivalent epoxide (1.4 to 1.6 mol HHDA per mol VCHDO). The resin obtained was very light yellow. The fully cured resin has a flexural modulus of 10^5 psi at 425°F. This resin should structurally resist skin temperatures up to 450°F in three-layer composite canopies.

Endomethylenetetrahydrophthalic anhydride, when used at ratios of 0.7 to 0.8 mol per mol equivalent epoxide as VCHDO, produces resins that have heat distortion temperatures above 525°F. Unfortunately cure temperatures of 550°F, which cause severe discoloration and oxidation of the resin, are required to obtain the high temperature resistance. This resin system is the most thermally rigid of all systems investigated to date.

The endomethylenehexahydrophthalic anhydride produces resins with heat-distortion temperatures in the 450°F range. However, when they are cured at temperatures above 500°F, rather severe degradation of thermal properties occurs.

A film-forming mold release agent was developed for releasing epoxide resins cast in plate glass molds. A water solution of 2.5 pph carboxymethylcellulose and 0.12 pph poly(vinyl alcohol), when coated onto the plate glass mold, forms a film that releases readily from the glass surface after the resins have cured. Castings of epoxide resins made in the coated plate glass molds had excellent optical properties.

The syntheses of novel epoxide resins are discussed. These resins are based on two bicyclic [2.2.1] heptane rings with three different types of connecting groups. These are a carbonate, an ester, and an ether. Thermal stability and color were of primary importance in selecting these structures. The endo bridging should add to the thermal stability of these resins and the three different connecting groups will help elucidate the color formation in these resins. A cured resin has been made using maleic anhydride, a polyol initiator and bis(bicyclo [2.2.1] -2-methyl-5,6-epoxy)carbonate. Physical properties of this resin were not determined.
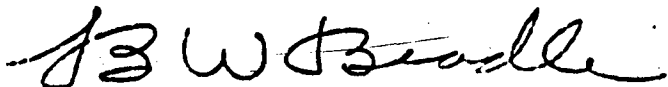
PREFACE

The work discussed in this report was carried out between 15 December 1959 and 14 February 1961 under the provisions of Contract NOas 60-6099-c for the Bureau of Naval Weapons, Department of the Navy. Mr. Mason Thompson of the Institute's Engineering Division was responsible for the stress-strain analysis, and establishment of evaluation procedures and instrumentation. Syntheses of the bicyclic diepoxide resins were carried out by Mr. Thomas Medved. Mr. Calvin Bolze, Chemical Statistician, carried out the analysis of data from the formula optimization experiments.

At the end of the normal contract period, sufficient project funds remained to support additional work. A request was made for an additional 60-day extension in the contract period, from 15 December 1960 to 14 February 1961. The request was granted 15 December 1960.

Mr. Howard Christie served as Project Leader under the supervision of Mr. Martin N. Schuler, Head, Industrial Chemistry Section. This report was prepared by Mr. Christie and Mr. Medved.

Approved for:

MIDWEST RESEARCH INSTITUTE

B. W. Beadle, Director
Chemistry Division

7 March 1961

TABLE OF CONTENTS

List of Tables

List of Illustrations

TABLE OF CONTENTS (Concluded)

List of Illustrations (Concluded)

LIST OF SYMBOLS

t_1 = temperature of oven air, °F.

t_2 = temperature of heated face, °F.

t_3 = temperature at interface, °F.

t_4 = temperature of cool face, °F.

t_5 = temperature of cool air, °F.

h_e = thermal conductivity of epoxy layer.

h_a = thermal conductivity of acrylic layer.

k_o = film coefficient of air on heated surface.

k_1 = film coefficient of air on cool surface.

x_e = thickness of epoxy layer, in.

x_a = thickness of acrylic layer, in.

q = heat flux in $Btu/ft^2/hr$.

CHEMICAL STRUCTURE DIAGRAMS

Trimethoxyboroxine (TMB)
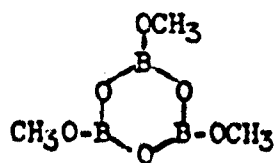
Diglycidyl ether of bisphenol A (DEBA)
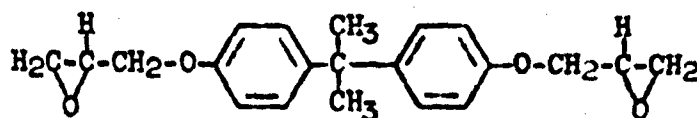
<u>3,4-Epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexanecarboxylate</u>
<u>(DDC)</u>
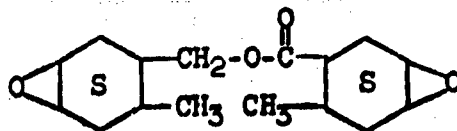
<u>6-methylbicyclo[2.2.1]-hep-5-ene-2,3-dicarboxylic anhydride (MEMTHPA)</u>
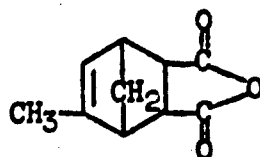
<u>Bicyclo[2.2.1]-hep-5-ene-2,3-dicarboxylic anhydride (EMTHPA)</u>
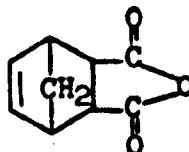
<u>Bicyclo[2.2.1]-heptane-2,3-dicarboxylic anhydride (EMHHPA)</u>
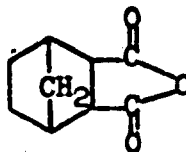
<u>Vinylcyclohexene dioxide</u>
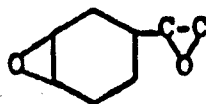
Dicyclopentadiene dioxide
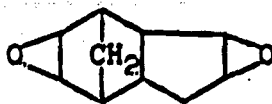
I. INTRODUCTION

The skin temperatures produced by air friction on supersonic aircraft are above the softening point (about 225°F) of the canopies in many operational supersonic aircraft. Hot-stretched acrylic is used for canopies because of its light weight, good optical properties, formability, and good resistance to crack propagation and impact failure. However, at temperatures above 225°F, regression of the stretched acrylic occurs.

At an altitude of 30,000 ft. the equilibrium skin temperatures are in the 250°F range at Mach 2, and in the 500°F range at Mach 3. The actual canopy skin temperatures will be somewhat lower because of internal cooling of the cockpit area, and geometrical configuration and location of the canopy. Use of hot-stretched acrylic in aircraft with speed capabilities above Mach 2 places a restriction on the length of time that the craft can be operated at maximum speed.

The initial objective of this program was an investigation into the mechanical properties of a two-layer composite canopy material. The composite consisted of an outer layer of a transparent thermoset plastic capable of resisting skin temperature of 400°F (minimum). A target goal of 500°F was established. Physical properties of the trimethoxyboroxine-cured diglycidyl-ether of bisphenol A were determined at room and elevated temperatures. An investigation into the distribution of stresses in a two-layer composite was carried out by instrumenting the composite with strain gauges and thermocouples.

Early in the project period, a number of 12 in. x 12 in. x 0.25 in. plates of the trimethoxyboroxine (TMB)-cured diglycidyl ether of bisphenol A (DEBA) were supplied to the Goodyear Aircraft Corporation. These plates were evaluated in a three-layer composite consisting of an outer layer of thermoset resin, a middle layer of an elastic thermoplastic, and an inner layer of hot-stretched acrylic. The results from shock-heating tests showed that the TMB-cured DEBA resin was superior to all other thermoset resins tested in respect to color stability at elevated temperatures and resistance to thermal shock.

The favorable results obtained by Goodyear led to some modification in the project goals. The three-layer composite produces a structure with less transfer of stress from the outer to inner layers than the two-layer composite, and thus should be more resistant to impact failure. Evaluation of the two-layer composite was suspended after the fourth month of the contract period. Emphasis was placed on mechanical evaluation of the TMB-cured DEBA resin and on the development of new resins from the saturated cyclic epoxides.

In addition, the level of effort expended on syntheses of some new bicyclic diepoxides was increased.

The work carried out on the anhydride-cured, saturated cyclic epoxides was aimed at the development of resins that would retain their strength at temperatures above 400°F, and also resist discoloration at these temperatures. Some of the resins obtained were more resistant than the TMB-DEBA resin to loss of physical strength and to discoloration at 400°F. Optimum ratios of anhydride to epoxide were determined for the materials investigated.

A film-forming water-soluble release agent suitable for releasing cured epoxide resins from plate glass molds was developed. This agent makes possible the production of castings with excellent optical surfaces.

This final report is divided into two sections. The first section covers the experimental work and results obtained from commercially available anhydrides and epoxide resins. The second section discusses the synthesis program aimed at preparation of a new class of epoxide resins based on bicyclic ring structures.

II. PLASTICS FROM COMMERCIALLY AVAILABLE MATERIALS

This section of the report is a presentation of the conclusions and a discussion (II A) of the results from the experimental work with commercially available materials that could be used to produce temperature-resistant, transparent composite plastics for supersonic aircraft canopies. II B is a description of the laboratory work carried out.

A. Conclusions Drawn From Experimental Results

1. Analysis of Strain Produced by Thermal Gradients Through Composites

Composite plates consisting of 0.25 in. thick layer of trimethoxyboroxine cured diglycidyl ether of bisphenol A cast against 0.25 in. poly-(methylmethacrylate) were instrumented with high-temperature strain gages and thermocouples at the innerface between the two layers and at each outer layer. The plates were subjected to air temperatures up to 450°F on the epoxy surface while they were cooled by a blast of room temperature air on the acrylic side. The effects of the temperature gradient on stress distribution through the

composite were measured. Analyses of the data indicate that the bending stresses were quite small, being 150 to 200 psi at an outer skin temperature of 350°F. This level of stress is considerably below the ultimate strength of the epoxy layer at temperatures up to 350°F.

2. Resins Cured with Trimethoxyboroxine

The work under Contract NOas 59-6137-c, "Development of High-Temperature Resistant Transparent Plastics", led to the use of trimethoxyboroxine (TMB), an organo-boron compound, as a catalyst for curing the diglycidyl ether of bisphenol A (DEBA). Five pph of TMB produced the most thermally stable resin and appeared to be the optimum catalyst concentration. The tensile and flexural properties of resins cured with 5 pph TMB at temperatures up to 220°F were determined. The strength levels were low and the resin lost strength at lower temperatures than expected.

A study of the effects of the concentration of TMB, cure temperature, and cure time indicated that the optimum catalyst concentration varied with cure time and temperature. Maximum thermal rigidity was obtained at a concentration of 6 to 7 pph TMB in DEBA. Table I is a summary of the tensile and physical properties of the resins obtained with a concentration of 6.5 pph TMB and a cure cycle of 3 hr. at 180°F, 4 hr. at 275°F, and 6 hr. at 350°F. The presence of an optimum amount of catalyst at 6.5 pph adds further weight to the hypotheses that the TMB acts as a Lewis acid-type catalyst for the etherification reaction between oxirane groups. Lee and Neville[1] reported on the use of TMB as a curing agent for epoxide resins. They propose an anhydride-type reaction to form a boron polyester.

During the first quarter of this project, several sheets of the TMB-cured DEBA were supplied to Goodyear Aircraft Corporation* for evaluation in a three-layer composite. The results[2] from these tests were quite promising. The sheets successfully passed the operational cycling test. The three-layer composite for canopies has some distinct advantages over the two-layer composite; impact resistance is higher, and the stress distribution caused by the temperature gradient is reduced. Some modification of the scope of this

---

* G.A.C. Plastics Engineering Department, Akron, Ohio. Attention Robert E. Shumaker.

1/ Lee, H., and Neville, K., "New Curing Agents for Epoxy Resins", SPE Journal, p. 315, March 1960.

2/ Quarterly Progress Report No. 4, "Evaluation of High Temperature Cast-in-Place Transparent Laminates Suitable for Canopies on Supersonic Fighter Aircraft", Contract NOas 59-6146-c, 9 February-8 May 1960, Goodyear Aircraft Corporation.

program was made after a meeting with the Bureau of Naval Weapons' project
monitor in May of 1960. Work with the two-layer composite was halted, and
an accelerated evaluation of the mechanical properties of the TMB-cured DEBA
resins was undertaken. In addition, the work on newer saturated cyclic
epoxides and syntheses of the bicyclic diepoxides was accelerated.

TABLE I

SUMMARY OF PHYSICAL PROPERTIES OF 6.5 pph TMB-CURED DEBA

| | Flexural | | Tensile | | |
Temp. ($^\circ$F)	Modulus of Elasticity in Flexure (psi x 10^{-5})	Ultimate Flexural Strength (psi)	Modulus of Elasticity in Tension (psi x 10^{-5})	Ultimate Tensile Strength (psi)	Elongation at Rupture (%)
76	5.33	20,800	5.77	13,100	1.99
150	4.02	17,600	4.79	11,500	2.48
200	3.10	11,970	3.58	7,000	3.78
250	1.48	5,500	1.70	5,000	2.01
280	0.70	2,000	0.30	-	-
300	0.26	670	-	-	-

Mixtures of the diglycidyl ether of bisphenol A and an epoxy novolak
could be cured with TMB to produce resins with better thermal rigidity than
with DEBA alone. A 60/40 mixture of these two epoxides produced a cured resin
with an E_b = 100,000 psi (flexural modulus is equal to 100,000 psi) tempera-
ture of 340°F. The epoxy novolaks are dark yellow. All attempts to decolor-
ize these materials have failed. The castings obtained were yellow, and would
not be at all suitable for aircraft canopies. If a colorless novolak can be
obtained, the cured resin would be greatly superior to the DEBA resin in
thermal stability and rigidity.

3. Anhydride-Cured Saturated Cyclic Epoxides

Vinylcyclohexene dioxide (VCHDO) was given a cursory evaluation
during the work carried out under Contract NOas 59-6137-c. Colorless resins
were produced with VCHDO and hexahydrophthalic anhydride (HHPA). However,
the use of VCHDO in preparing two-layer composite plate was not possible be-
cause of severe attack of the poly(methylmethacrylate) by the VCHDO. As the
outer layer of the three-layer composite will be cast separately, no limita-
tions are placed on selection of the resin components by the presence of the
acrylic layer.

Of the three anhydrides, hexahydrophthalic (HHPA), endomethylene-tetrahydrophthalic (EMTHPA) and endomethylenehexahydrophthalic (EMHHPA) investigated, EMHHPA yielded the most color-stable resin. The drop in light transmission of a 0.25 in. thick sheet soaked at 410°F (210°C) was only 1.75×10^{-2} per cent per minute. The TMB-cured DEBA had a rate of 6.16×10^{-2} per cent per minute at 400°F (204°C). The optimum ratio on EMHHPA to VCHDO was 0.7 to 0.8 mol equivalent anhydride per mol equivalent VCHDO. When catalyzed with 0.25 pph of a 60 per cent aqueous solution of benzyltrimethylammonium chloride, a resin with an $E_b = 100,000$ psi temperature of 400°F was obtained. On exposure the 550°F severe thermal degradation of this resin occurred. However, this resin looks most promising for use in three-layer composite canopies at temperatures of 400° to 450°F.

Hexahydrophthalic anhydride and VCHDO produced a resin with an $E_b = 100,000$ psi temperature of 420°F when catalyzed with 0.6 pph of the quarternary amine salt and post-cured at 450°F. At this high catalyst concentration, the cured castings were yellow prior-to-post cure. When the catalyst level is lowered to 0.30 pph, the color formation is substantially reduced but the $E_b = 100,000$ psi temperature is reduced to 380°-390°F. The discoloration rate on exposure of 0.25 in. thick sheet to 410°F is 3.75×10^{-2} per cent per minute, nearly half that of the TMB-DEBA resin at 400°F. The optimum ratio of HHPA to VCHDO was 0.7 to 0.8 mol equivalent anhydride per equivalent VCHDO. The resin obtained from HHPA and VCHDO should be usable in canopies at temperatures up to the 400°-425°F range.

The most thermally rigid resin was obtained from VCHDO and endo-methylenetetrahydrophthalic anhydride (EMTHPA). This mixture could be cured to $E_b = 100,000$ psi temperatures of 540°F (282°C). Unfortunately, this anhydride yields a highly colored cured resin even at post-cure temperatures not exceeding 350°F. The anhydride was carefully distilled through a five-plate bubble cap column in an attempt to reduce the color formation. No great reduction in color was obtained.

Other attempts to purify the EMTHPA met with similar failure. The resin obtained from this anhydride and VCHDO is the most thermally stable of all resins investigated having a weight loss of only 5.3 per cent after 32 hr. at 500°F. The VCHDO-HHPA resin lost 12.5 per cent after the same exposure.

4. Film-Forming Mold Release Agent For Glass

Excellent release of cured epoxide resins from plate glass has been obtained by the use of a film-forming release agent. A water solution of 2.5 pph low-viscosity-grade carboxymethylcellulose and 0.5 pph of a viscosity-grade poly(vinyl alcohol) flushed onto polished plate glass and dried, produced

an excellent release film. The film is completely transparent, very smooth, and has the proper degree of adhesion to the glass surface.

Excellent release is obtained with amine, anhydride, and catalytically TMB-cured DEBA resins. More care is required in preparing coated molds for resins based on VCHDO because of the very low viscosity and solvent action of this low molecular weight compound.

B. Experimental

1. Preparation and Testing of Two-Layer Composites

The following discussion reviews the procedure used for the preparation of the epoxy-acrylic composites.

a. **Surface preparation of acrylic layer**: The surface of the acrylic sheet was cleaned with a refined kerosene of low aromatic content to remove all traces of the masking paper adhesive. The sheet was then washed in warm detergent solution, thoroughly flushed with distilled water, and dried. This procedure has been found satisfactory in terms of both adhesion and solvent stress crazing.

b. **Mold preparation**: Gaskets of the desired thickness are made from a commercial room temperature vulcanizing silicone rubber. The gasket is placed between the acrylic sheet of the composite and an additional sheet of acrylic that has been flush-coated with a poly(vinyl alcohol) solution. Spring clamps are placed at the gasket line. Three sides and about one-half of the top of the mold are sealed by the gasket.

Care must be used in coating the sheet with poly(vinyl alcohol) in order to provide a smooth mold release film. The solution used was a 5 per cent concentration of a medium viscosity grade poly(vinyl alcohol) in water. The solution was filtered prior to use to remove any particulate contamination. The coated plate was then placed in an oven at 180°F to dry the release film.

c. **Preparation of epoxy resin**: The diglycidyl ether of bisphenol A* was heated to 140°F, degassed at <5 mm. Hg and 5 per cent by weight trimethoxyboroxine* was thoroughly mixed into the resin. The mixture was then carefully poured into the mold. An alternate method in which the resin is

---

* See List of Symbols for structures.

injected at the bottom of the mold insures that no air bubbles will be entrapped in the casting.

        d. <u>Curing</u>: The acrylic layer determines the upper-temperature limit for curing the resin. The maximum temperature used in preparing the composite discussed is 200°F.

        The filled mold was placed in a forced air circulating oven at 200°F for a period of 18 hr. After this period, the mold was removed and the composite separated from the gasket and mold sheet. The Barcol* hardness of the epoxy layer should read at least 45 with no flow. If the hardness is not high enough or if cold flow is indicated, the composite is returned to the oven until these values are obtained.

        After curing, the poly(vinyl alcohol) mold release film was washed from the composite.——Warm water containing a small amount of detergent readily removes the film.

        e. <u>Test equipment and procedures</u>: An electrically-heated test oven was modified so that it could be used to produce the desired thermal gradient through 6 in. sq. composite specimens. The composite specimens were mounted in the window space with the epoxy layer facing into the oven. The outer surface temperature of the composite was cooled by a stream of room temperature air passing over this surface. This arrangement of equipment provided a means of controlling the thermal gradient through the composite and allowed a reasonable reproduction of cockpit conditions.

        f. <u>Determination of heat transfer through the acrylic-epoxy composite</u>:

        (1) <u>Theoretical considerations</u>: The initial determination of the heat transfer characteristics of the acrylic-epoxy composite was performed to determine the thickness of materials required to produce the necessary temperature gradient through the composite. The information was also required for design of subsequent test equipment and procedures. The temperature requirements which the composite must meet include a minimum outer face temperature of 400°F and an inner face temperature not exceeding 180°F to 225°F (i.e., the hot-stretched acrylic must be kept below its relaxation temperature). The temperature gradient through a typical composite cross section is shown in Fig. 1.**

---

*   Barber-Colman Impressor, Model No. GY2T-934-1.

** See p.viii for explanation of symbols.

EPOXY LAYER

K_o, FILM COEFFICIENT

t_1

t_2

K_i, FILM COEFFICIENT

t_3

t_4

t_5

t_6

t_e
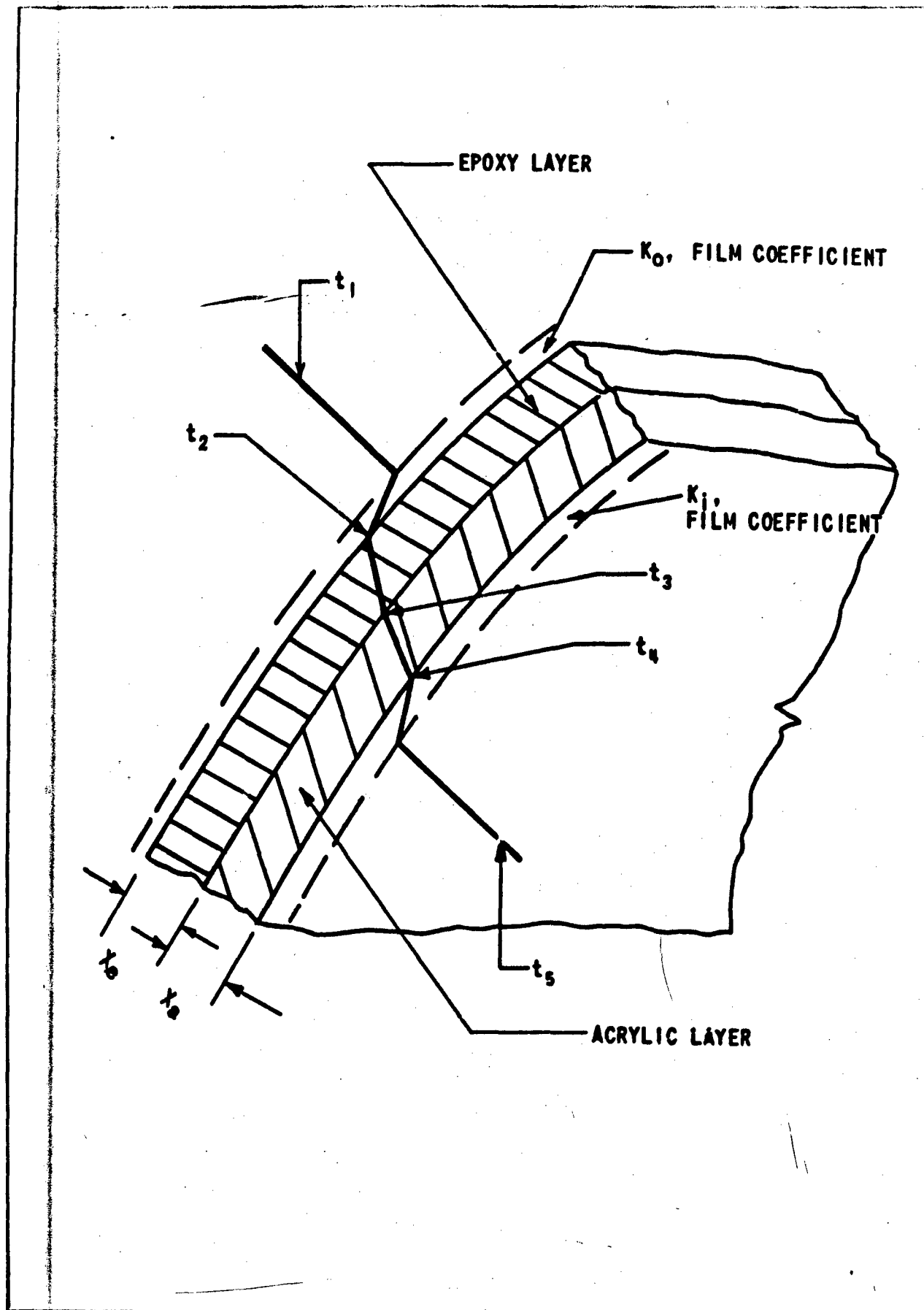
ACRYLIC LAYER

Fig. 1 - Temperature Gradient Through Composite

Four heat flow equations from Fig. 1 are as follows:

$$kq_{1-2} \text{ (heated air film)} = k_o(t_1-t_2)$$

$$q_{2-3} \text{ (epoxy layer)} \quad = \frac{h_e}{x_e}(t_2-t_3)$$

$$q_{3-4} \text{ (acrylic layer)} \quad = \frac{h_a}{x_a}(t_3-t_4)$$

$$q_{4-5} \text{ (cool air film)} \quad = k_1(t_4-t_5)$$

These equations are applicable for solution only if all values are known. The minimum outer face (t_1) and inner face (t_3) temperatures can be assumed as 400° and 180°F, respectively. The film coefficient (k_1) between the cockpit air and the acrylic face at low air velocity was assumed as 6 Btu/hr/ft^2/°F.

The thermal conductivity of the epoxy and acrylic layers of the composite were known only approximately for the temperature ranges to be encountered. For these reasons and because the film coefficients of the air flow on the two composite surfaces are known only in general terms, the results of these calculations were not used as a firm basis for design of the composite.

Using 1.30 Btu/hr/ft^2/°F/in for the thermal conductivity (h_a) for the acrylic and 1.00 Btu/hr/ft^2/°F/in for thermal conductivity of the epoxy layer, solution of the four equations showed that approximately 1/2 in. layer of epoxy would be required to adequately protect the acrylic layer at minimum temperatures. The results from these calculations are presented in Table II.

(2) Experimental determination of h_u and h_e: A composite instrumented with 28 gage iron-constantan and Baldwin SR-4 strain gages was prepared. The thermocouple and strain gages were bonded to the inner face of the acrylic prior to casting the composite. A mixture of 10 pph diethylene-triamine in the diglycidyl ether of bisphenol proved adequate for bonding to the acrylic sheet.

TABLE II

CALCULATED AND EXPERIMENTAL THERMAL EQUILIBRIUM OF EPOXY-ACRYLIC COMPOSITES

| Notation | Calculated Thermal Properties | | | | | | Experimental Thermal Properties | | | |
| | Condition 1 | | Condition 2 | | Condition 3 | | Test 1 | | Test 2 | |
	Acrylic	Epoxy	Acrylic	Epoxy	Acrylic	Epoxy	Acrylic	Epoxy	Acrylic	Epox.
x_a = acrylic thickness, in.	0.25	--	0.325	--	0.325	--	0.24	--	0.24	--
x_e = epoxy thickness	--	0.50	--	0.625	--	0.675	--	0.325	--	0.325
t_5 = cool air temp., °F	80	--	80	--	50	--	--	80	--	80
t_4 = cool surface temp., °F	120	--	120	--	100	--	--	120	--	115
t_3 = interface temp., °F	170	170	184	184	180	180	232	232	226	226
t_2 = hot surface temp., °F	--	300	--	350	--	400	--	315	--	310
t_1 = hot air temp., °F	--	340	--	390	--	450	--	402	--	399
k_1 = cool surface film coeff., Btu/°F/ft²/hr	6.5	--	6.5	--	6.5	--	15.2	--	19.6	--
k_o = hot surface film coeff., Btu/°F/ft²/hr	--	6.5	--	6.5	--	6.5	--	7.08	--	6.87
h_a = thermal cond. of acrylic, Btu/°F/in/ft²/hr	1.32	--	1.32	--	1.32	--	1.32	--	1.32	--
h_e = thermal conductivity of epoxy, Btu/°F/in/ft²/hr	--	1.00	--	1.00	--	1.00	--	2.42	--	2.36
q = heat flow, Btu/hr	260	260	260	260	325	325	616	616	611	611

After the composite was cured, thermocouples and strain gages were bonded to the epoxy and acrylic surfaces. Trimethoxyboroxine-catalyzed-epoxy resin was used for bonding the gage and thermocouple to the epoxy (high temperature) side, the amine and resin were used on the acrylic side. A considerable amount of effort was required to develop satisfactory methods for transfer and mounting of the strain gages. An instrumented composite test specimen is shown in Fig. 2.

The instrumented composite was placed in the oven window and subjected to increasing temperatures. The temperature through the composite was monitored and final readings were taken after 5 min. at equilibrium temperatures. Both temperature and strain readings were obtained. These data were used to calculate heat flux through the composite. Data from this experiment are shown in Table II.

On the basis of these tests it was estimated that the epoxy layer will need to be approximately 5/8 in. thick to provide the required protection for the hot-stretched acrylic layer.

g. Analysis of strain produced by the thermal gradient through the composite: The instrumented composite held three Baldwin CD-7, SR-4 type strain gages, one each on the exterior surfaces and one at the epoxy-acrylic interface (see Fig. 2). The strain produced at the three locations was recorded with the equilibrium temperature readings. The strain readings from this test and a duplicate test are presented in tabular form in Table III and in graphical form in Figs. 3 and 4.

The strain measurements shown (E_2, E_3 and E_4) represent the strain on the surfaces and interface corresponding to the thermocouple positions. The gages used on this instrumented composite were mounted on a phenolic film that softens above 350°F. This fact placed some doubt on any data taken above that temperature. The bending strain produced in the composite layers can be represented as half the differences in strains on the extreme fibers. The bending strain obtained from these corresponds to a relatively low level of 150 to 200 psi bending stress.

2. Physical Properties of the TMB-Cured DEPA Resin

a. Preparation: The sheets of cured resin used to make the tensile and flexural test specimens were prepared as follows:

(1) As-cast acrylic sheets, 13 in. by 13 in. by 1/4 in. were cleaned and flush-coated with a 5 per cent solution of poly(vinyl alcohol).

Fig. 2 - Strain Gage Instrumented Composite

TABLE III

STRAIN AND THERMAL GRADIENT IN EPOXY-ACRYLIC COMPOSITE DURING DIFFERENTIAL HEATING

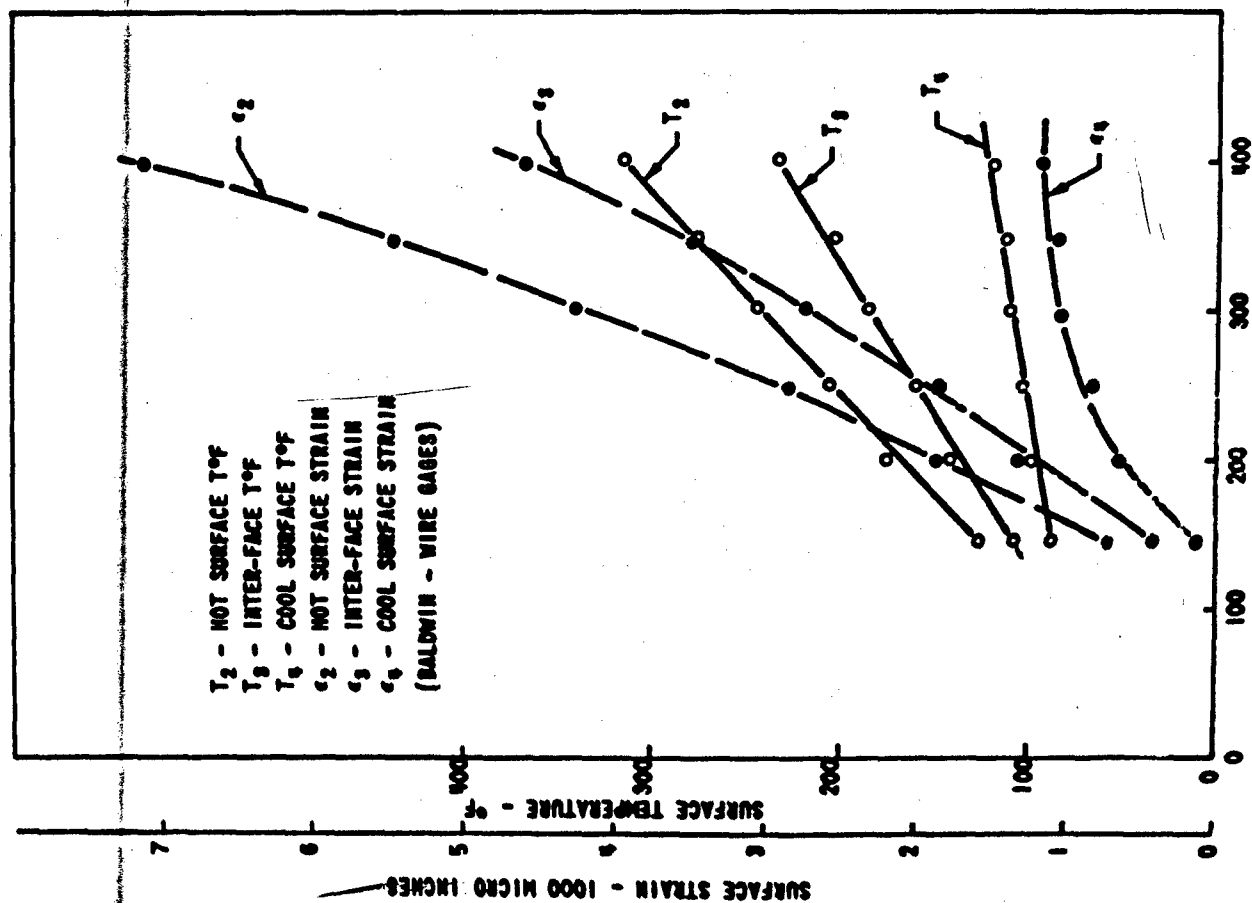| Oven Temp. T_1°F		Laminate Temperature							Laminate Strain					
		Hot Surface T_2°F		Interface T_3°F		Cool Surface T_4°F		Room Temp. T_5°F	Hot Surface ϵ_2 (in.)		Interface ϵ_3 (in.)		Cool Surface ϵ_4 (in.)	
a	b	a	b	a	b	a	b		a	b	a	b	a	b
92		90		88		85	85	80	--	--	--	--	--	--
150	153	125	126	106	107	86	85	80						
148	153	126	125	108	108	87	87	80						
149	155	126	126	110	108	88	87	80						
(149)	(154)	(126)	(126)	(108)	(108)	(87)	(86)	(80)	+ 720	+ 800	+ 430	+ 500	+ 140	+ 210
	200		158		128		90	80						
201	200	175	162	142	130	99	91	80						
201	198	174	161	142	131	99	92	80						
(201)	(199)	(175)	(160)	(142)	(130)	(99)	(91)	(80)	+1,870	+1,860	+1,310	+1,090	+ 680	+ 44
250	245	203	194	159	152	102	97	80						
248	247	205	196	160	153	104	98	80						
254	250	206	193	160	152	100	97	80						
(251)	(247)	(205)	(194)	(160)	(153)	(103)	(97)	(80)	+2,840	+2,530	+1,840	+1,570	+ 820	+ 720
302	304	243	234	184	176	107	103	80						
305	300	245	234	185	177	110	103	80						
306	298	245	234	185	177	109	103	80						
(304)	(301)	(244)	(234)	(185)	(177)	(109)	(103)	(80)	+4,250	+3,730	+2,740	+2,400	+1,040	+ 940
	350		272		201		108	80						
350	351	275	273	204	201	113	109	80						
349	350	275	273	204	202	112	109	80						
(350)	(350)	(275)	(273)	(204)	(201)	(112)	(109)	(80)	+5,450	+5,190	+3,420	+3,390	+1,055	+1,140
400	400	313	310	234	225	120	115	80						
397	399	315	309	232	226	120	115	80						
405	398	312	311	232	226	120	114	80						
(401)	(399)	(313)	(310)	(233)	(226)	(120)	(115)	(80)	+7,110	+6,390	+4,580	+5,250	+1,160	+1,070

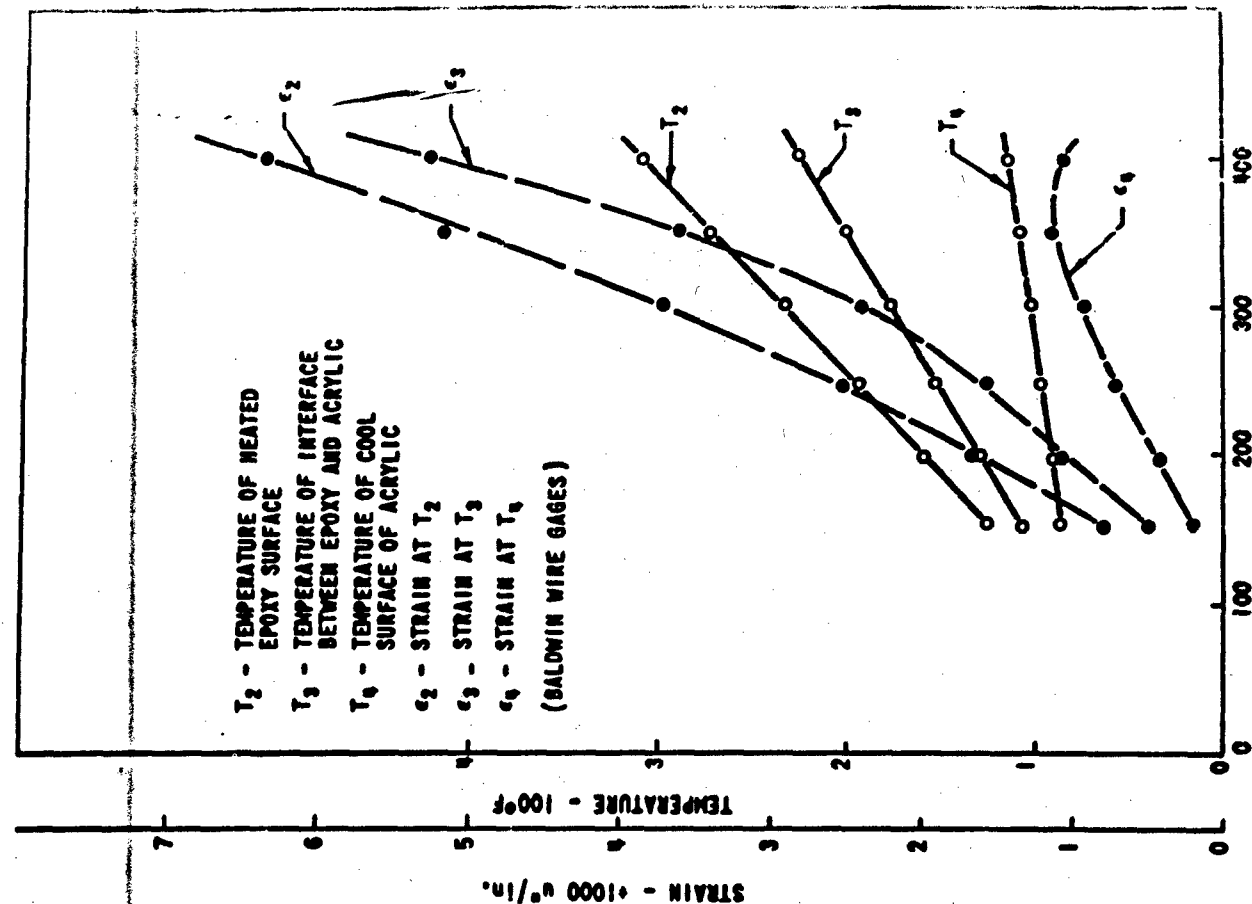Fig. 4 – Temperature and Strain Distribution through Laminate Exposed to Heat Flux

Fig. 3 – Temperature and Strain Distribution through Laminate Exposed to Heat Flux

The coating was dried at 140°F. One-fourth inch thick silicone-rubber gaskets were placed between the coated sheets and held together with spring clamps.

(2) The diglycidyl ether of bisphenol A (DEBA) was heated to 160°F, 5 pph trimethoxyboroxine (TMB) was added and thoroughly mixed into the resin. The resin mixture was filtered into the mold through a funnel containing loosely packed unbonded fibrous glass. The filtering removed any scum or gelatinous particles formed during addition and mixing of the resin and catalyst.

(3) The filled mold was placed in an oven and cured for 18 hr. at 180°F. After cooling the mold was separated from the cast epoxy sheet. The poly(vinyl alcohol) release film was washed from the sheet with lukewarm water. A number of sheets were cast to provide a sufficient quantity of material for making the flexural and tensile test specimens.

b. **Test equipment:**

(1) **Flexural test fixtures:** Flexural properties of TMB-DEBA were investigated at elevated temperatures using the temperature test oven mounted on the Institute's Instron Testing Machine (Type TT-CM) (see Fig. 5). In order to conduct these flexural tests with this oven arrangement, the tensile grip fixtures were replaced with a center loading, simple beam, flexural test fixture shown in Fig. 6. The fixture was designed to conform to the ASTM Standards for Tests of Flexural Properties of Plastics (D 700-58T), with a specimen beam length of 16t (16 times the thickness of the specimen). In order that several thicknesses of sheet plastic may be tested using this fixture, four sets of holes are provided covering a range of specimen lengths of 2, 4, 8, and 10 in. (specimen thickness from 1/8 to 5/8 in.).

Flexural test specimens conforming to the above noted ASTM Method of Test (D 700-58T) were machined from four 12-in. square sheets of 0.25 in. thick cast sheets. The specimens, 1/2 in. wide and 6 in. long, were carefully machined with light cutting strokes of the cutting head, and water as a lubricant and cooling fluid, to minimize residual stresses from the machining operation. After machining, the test specimens were stress relieved at 350°F for 30 min.; then examined by viewing through a sheet of Polaroid plastic so that residual stresses, stress concentration, nicks or voids, and uneven mixing of the resin would be distinguished by polarized fringe patterns. Specimens exhibiting an appreciable amount of fringe indexes from any of the above causes were discarded and not used. It was not possible to obtain all specimens free of any fringe patterns; however, the fringe patterns remaining in the specimens used were of low order fringes and principally parallel to the span of the bend specimen (not normal to the load application of the
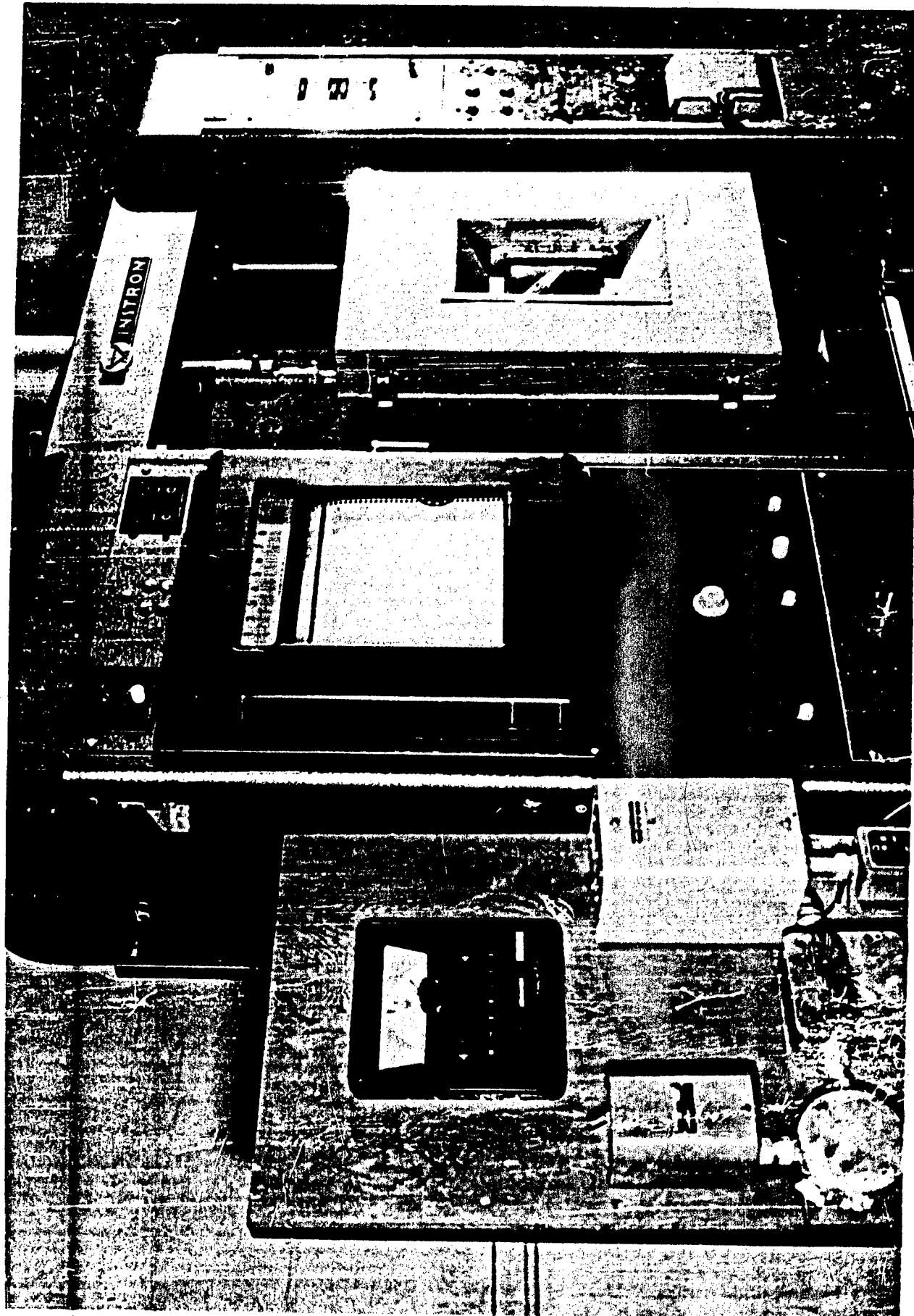
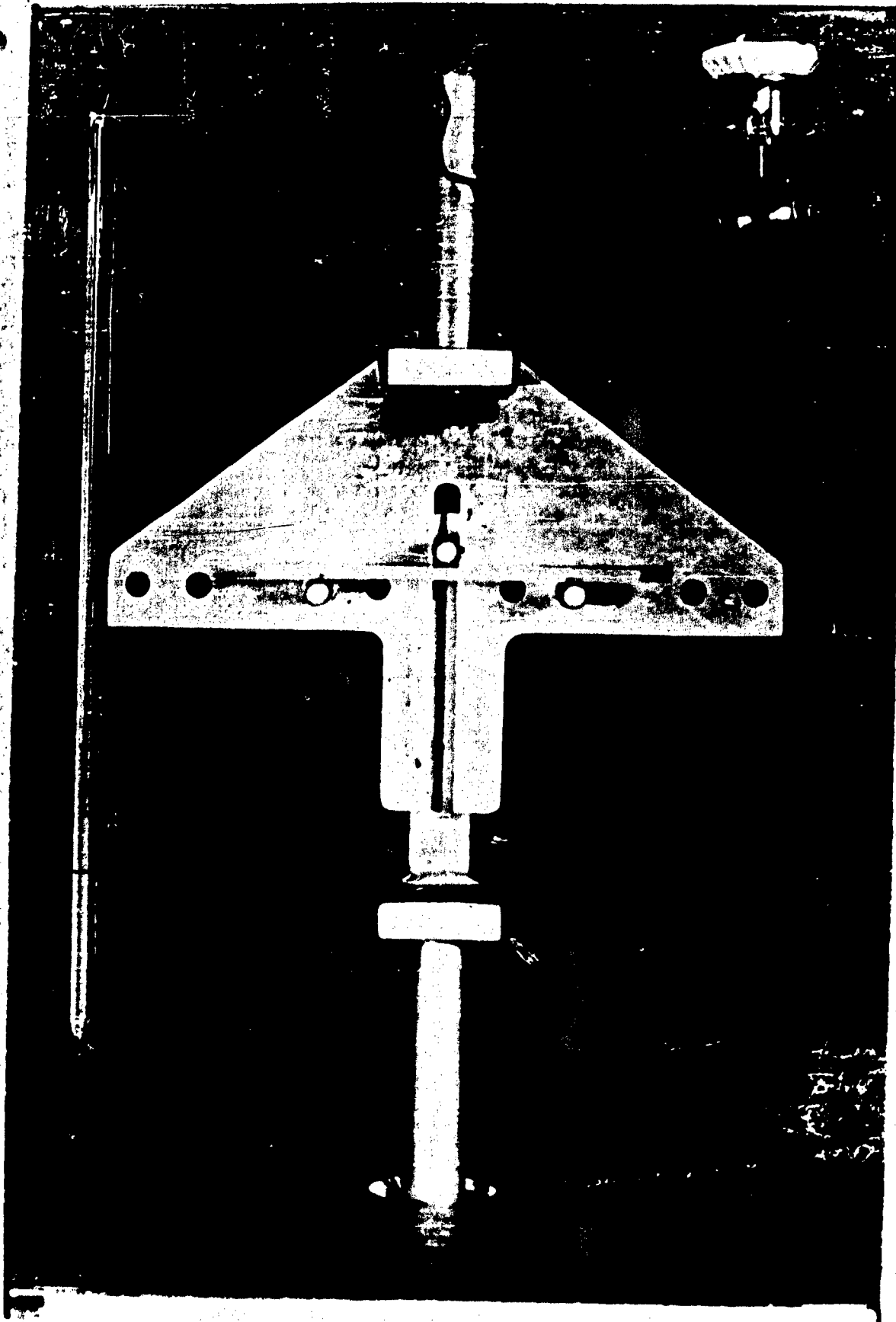Fig. 5 - High Temperature Test Oven and Controller

Fig. 6 - Flexural Test Fixture

specimens in bending), so that these fringes should have little effects on the test data.

The mid-span bending load was applied to the test specimens at a uniform crosshead rate of 0.20 cm/min (the nearest metric crosshead rate, on the Institute's Instron Testing Machine, corresponding to the 0.10 in/min specified by ASTM D 700-58T). A load deflection record of each specimen was recorded on the Instron's pen recorder. The elevated temperature of the test oven and test specimens was regulated and measured by a temperature regulator (Sim-Ply-Trol) and thermocouple bridge.

The measuring thermocouple was embedded in a section of cured resin sheet duplicating the test specimen and placed adjacent to the test specimen. When the measuring thermocouple indicated that stable temperature had been reached, the test was carried out. The temperature indicated by the thermocouple was recorded as the test temperature.

(2) Tensile test fixtures: The initial tests were carried out with wedge type grips (see Fig. 7) and an extensometer that was sensitive to any bending moment placed on the tensile test specimen during testing. Considerable deviation in test data was produced by this system because slippage of the jaws placed an eccentric load on the test specimen, and the specimen bent. These phenomena were the cause of erratic and inaccurate strain readings. A modified extensometer was built and the wedge jaws replaced with a perpendicular clamp type jaw. The data obtained with this equipment were much more consistent and are considered reasonably reliable.

The extensometer, shown in Fig. 8, was equipped with a temperature stable Schavitz transformer to sense strain of the specimen during loading. The strain output of the Schavitz transformer was fed first to a Daytronic Corporation, Model 300, Displacement Indicator for calibration and then to the axis input of a Moseley, Autograf, X-Y Recorder. The load signal from the Instron was applied to the Y-axis input of the recorder. The recording obtained was a direct reading stress-strain curve for the specimen under test.

Tensile test specimens were prepared according to ASTM D 638-58T, "Tests for Tensile Properties of Plastics". The specimens were machined from 0.25 in. nominal thickness sheets of the cured resin using cutting and stress-relieving techniques previously described. The nominal dimensions of these test specimens included a 1/2 in. constant width test section, a gage length of 2-7/8 to 3 in. and a grip area of 3/4 to 7/8 in. in width with a total length of 6.0 in.
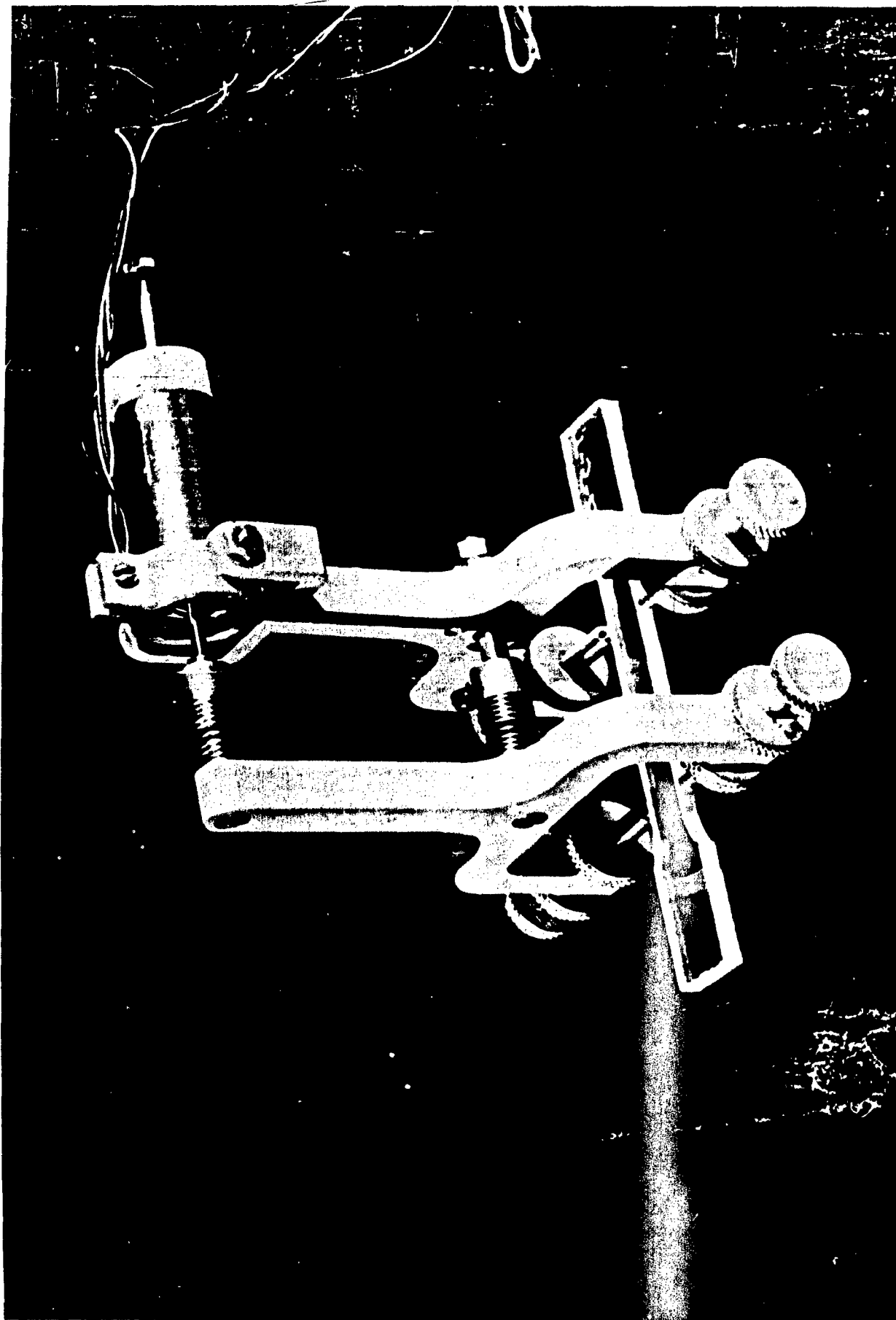
Fig. 7 - Test Grips and Activating Rods

- 19 -

Fig. 8 - Extensometer and Test Specimen

The specimen loading rate of 0.5 cm/min (0.197 in/min) used is in close agreement with ASTM D-638-58T. The tests were carried out at room and elevated temperatures. The elevated temperature tests for tensile properties followed the procedure outlined for determining the temperature during measurement of flexural properties.

c. **Properties of DEBA resin cured with 5 pph TMB**: The initial tests were made on sheet castings of DEBA cured with 5 pph TMB. The sheets were prepared as outlined in Section II-C-2a. These specimens were cured at 220°F for 6 hr. following the 18 hr. at 180°F cycle. Tensile and flexural test specimens were prepared from the cured sheets and tested as previously outlined. The data obtained are shown in Figs. 9 and 10.

d. <u>Catalyst concentration and cure cycle optimization</u>: There were some discrepancies between the temperature at which a large strength loss (transition temperature) occurred that was previously reported and those found during this report period. These changes suggested that the formulation was extremely sensitive to elevated temperatures and to the time from initial cure to the annealing operation. Apparently the resin was not completely cured, either from too low a catalyst concentration or an incomplete cure cycle.

A study of the effects of the concentration of TMB and cure cycle on the thermal resistance of the cured epoxy resin was carried out. Four levels of TMB concentration were used, 4, 6, 7, and 9 parts TMB per 100 parts of the diglycidyl ether of bisphenol A (DEBA). Three post-curing temperatures, 300, 350, and 400°F, and three post-cure times, 4, 16, and 50 hr., were used to cure the resin-catalyst mixture.

After the appropriate cure cycles were completed, flexural test specimens were cut from the cured sheets. These specimens were 0.5 in. wide, approximately 0.25 in. thick, and 6.0 in. long. The flexural modulus (E_b) of each specimen was determined at increasing temperatures until the modulus was below 1×10^5 psi. Figures 11, 12, and 13 show the effects of catalyst concentration, cure temperature, and cure time on the thermal resistance of the cured resin. These figures are plots of the temperature at which the flexural modulus of elasticity (E_b) is equal to 10^5 psi. The numerical data are given in Table IV.

The data obtained from this experiment were subjected to a statistical analysis to determine if the effects observed were significant.
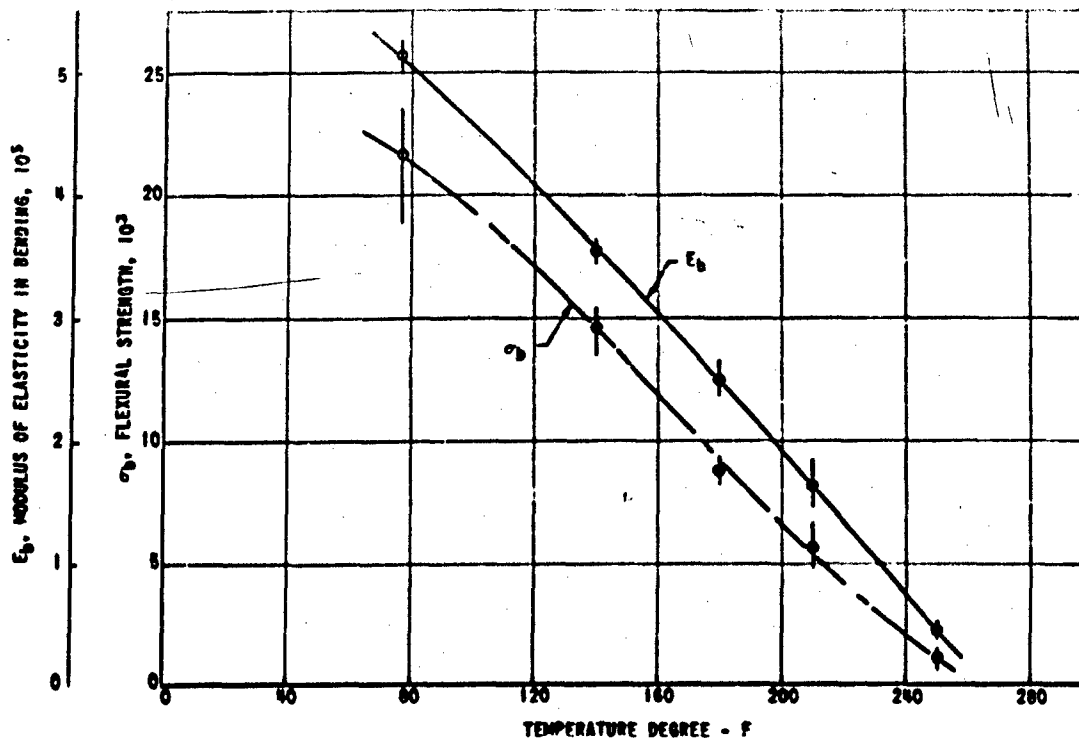
Fig. 9 - Flexural Strength and Modulus of Elasticity in
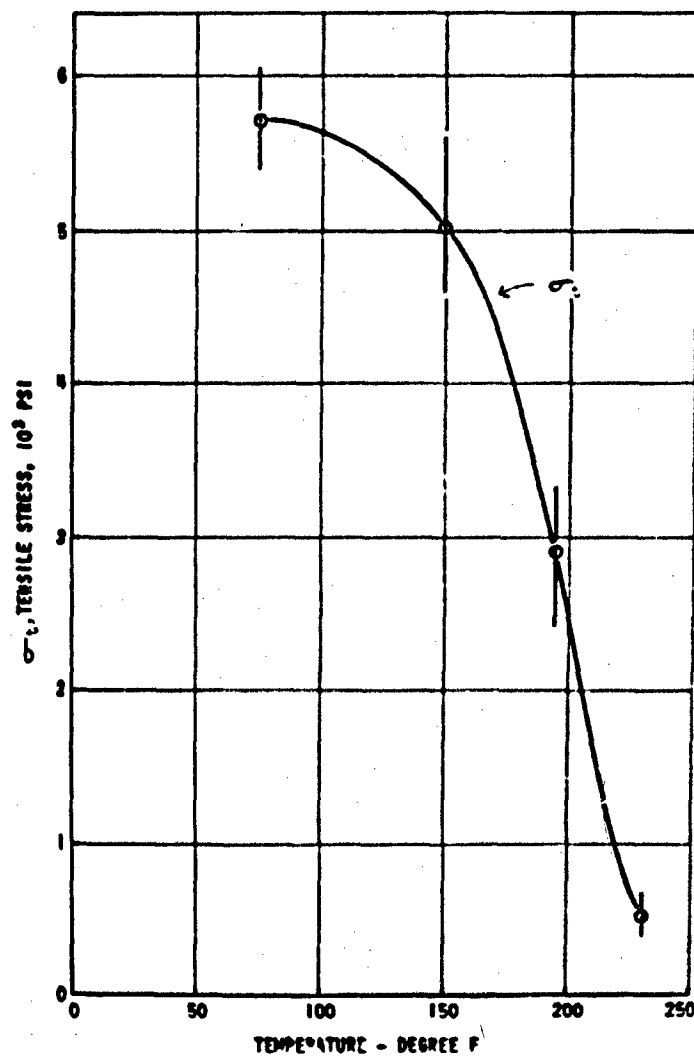Bending vs. Temperature

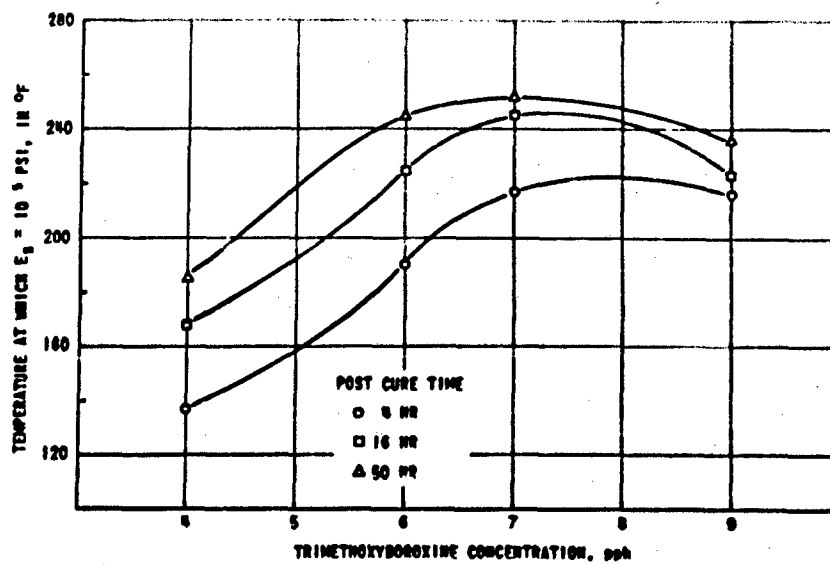Fig. 10 - Maximum Tensile Stress vs. Temperature

Fig. 11 - Effect of Catalyst Concentration at 300°F
Post-Cure on Thermal Resistance
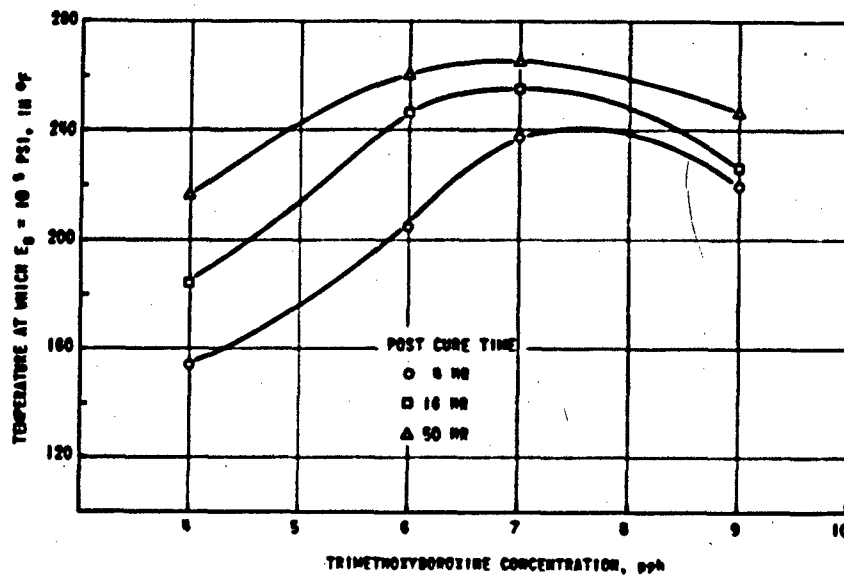
Fig. 12 - Effect of Catalyst Concentration at 350°F
Post-Cure on Thermal Resistance
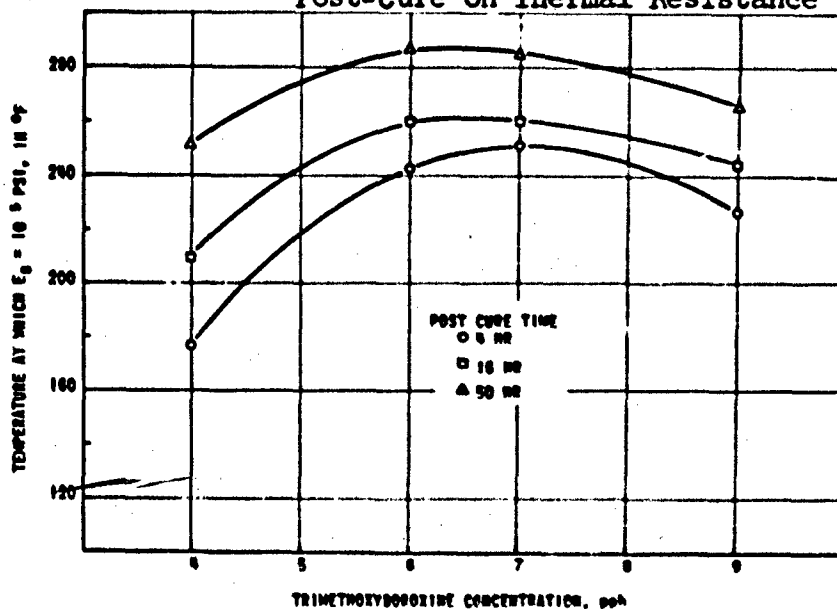
Fig. 13 - Effect of Catalyst Concentration at 400°F
Post-Cure on Thermal Resistance

TABLE IV

EFFECT OF CATALYST CONCENTRATION AND CURE CYCLE ON FLEXURAL STRENGTH AT ELEVATED TEMPERATURES

TMB Concentration (pph)	Cure Time (hr.)	Temperature at which $E_b = 100,000$ psi Cure Temperature (°F)		
		300	350	400
4	4	138	155	176
	16	168	185	210
	50	185	217	251
6	4	190	225	242
	16	225	246	260
	50	245	261	287
7	4	218	238	252
	16	246	255	260
	50	252	265	285
9	4	217	220	228
	16	223	225	245
	50	237	246	267

A second order model was fitted to the data by the least squares method. The form of this surface would be:

$$T(E_b=10^5) = \omega + b(C) + c(C^2) + d(t) + e(t^2)$$

$$+ f(T) + g(T^2) + h(tC) + i(TC)$$

$$+ j(tT)$$

where   C is catalyst concentration in per cent

t is logarithm of time

T is temperature in °F.

As the levels were not equally spaced in terms of the transformed variables, it was necessary to compute the following orthogonal comparisons for analysis.[1]

C	4	6	7	9
C_L	-5	-1	+1	+5
C_Q	+1	-1	-1	+1

T	300°	350°	400°
T_L	-1	0	+1
T_Q	+1	-2	+1

t	4	16	50
t_L	-17	1	16
t_Q	5	-11	6

The equation in terms of these variables was:

$$T_{(E_b=10^5)} = 227.50 + \underline{4.82}\ C_L - \underline{18.61}\ C_Q + \underline{1.26}\ t_L + 0.04\ t_Q$$

$$+ \underline{19.58}\ T_L + 0.00\ T_Q - \underline{0.10}\ C_L t_L - \underline{1.96}\ C_L T_L$$

$$- 0.04\ t_L T_L$$

Using the residual as the estimate of experimental error, the coefficients were tested for statistical significance. The underlined coefficients were very highly significant ($p = 0.999$). The other coefficients were not significant at the 0.95 level.

Examination of the above equation shows the following:

1. At a given cure temperature and time, an optimum catalyst concentration exists.

2. If cure time or temperature is increased, the optimum catalyst concentration is decreased.

3. The effect of increasing cure time or cure temperature (at a given catalyst concentration) is to increase the $T_{(E_b=10^5)}$.

4. There is no evidence of a maximum in either cure time or cure temperature and the variables appear independent in this range.

---

[1] Robson, D. S., "A Simple Method for Constructing Orthogonal Polynomials when the Independent Variable is Unequally Spaced", Biometric, Vol. 15, No. 2, 187-191.

e. Determination of the tensile and flexural properties of DEBA
resin cured with the optimum concentration of TMB: A number of 13 x 13 x
1/4 in. plates of the 6.5 pph TMB-DEBA resin were prepared. The cure cycle
used was 3 hr. at 180°F, 4 hr. at 275°F, and 6 hr. at 350°F. Sixteen of
these plates were forwarded to the Goodyear Aircraft Corporation, Akron, Ohio,
for evaluation. The remaining plates were cut into flexural and tensile test
specimens for determination of physical properties at elevated temperatures.
The tests carried out have been described previously. The data from these
tests are shown in Tables V, VI, and VII, and in Figs. 14, 15, and 16.

f. Improvement of thermal resistance with an epoxy novolak: The
strength of the TMB and DEBA drops rapidly at temperatures between 275 and
300°F. It is desirable that the material resist temperatures up to 400°F.
An investigation of a polyfunctional epoxide resin derived from a phenolic
novolak was carried out. This material having a much higher reactive func-
tionality than the diglycidyl ether of bisphenol A produces a cured resin of
higher heat distortion temperature.

The structural diagram of this resin is shown below:
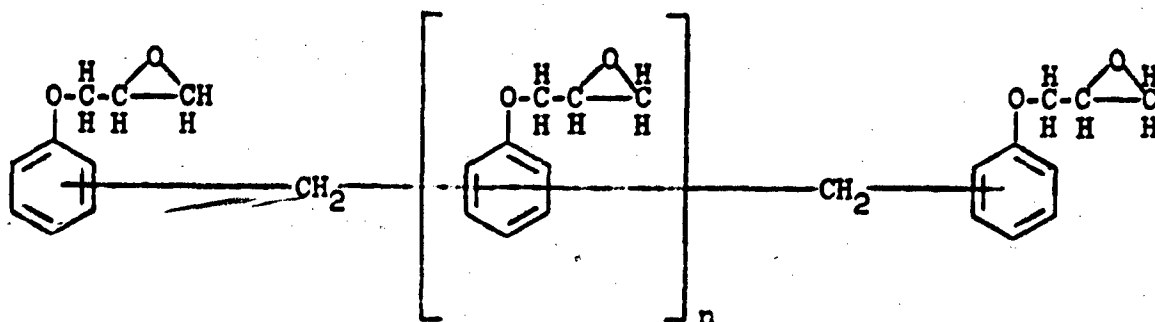
The value for n ranges from 0 to 3 with an average value of 1.3. The pres-
ence of more epoxy groups increases the reactivity of the monomer and thermal
stability of the cured resin. The commercially available resin has a color
of 5 on the Gardner-Holt scale and a viscosity of approximately 50,000 cps at
125°F. The resin is too high in viscosity to be used directly and must be
blended into the diglycidyl ether of bisphenol A (DEBA).

TABLE V

FLEXURAL PROPERTIES OF EPOXY RESIN AT ELEVATED TEMPERATURES
(6.5 pph TMB in DEBA, Cure Cycle 18 hr. - 180°F, 12 hr. - 350°F)

Spec. No.	Width (in.)	Thickness (in.)	Max. Load (lb.)	Ultimate Flexural Strength (σ_b, psi)	Modulus of Elasticity E_b, psi x 10^{-5}
Room Temperature, 77°F					
1	0.4970	0.2320	95.9	21,520	5.65
2	0.5025	0.2621	131.2	22,800	5.27
3	0.5050	0.2791	89.3	13,650 [1]	5.32
4	0.4967	0.2317	54.7	12,320 [1]	5.42
5	0.4990	0.2243	94.3	22,560	5.26
6	0.4958	0.2546	109.3	20,400	5.22
7	0.5044	0.2267	78.3	16,800	5.17
Avg.				20,810	5.33
Std. Dev.				±2,370	±0.14
Temperature 150°F					
1	0.5013	0.2697	114.0	18,350	3.97
2	0.4984	0.2505	68.4	13,120 [2]	2.86 [2]
3	0.4980	0.2206	70.6	17,400	4.10
4	0.5005	0.2550	100.8	18,600	4.01
5	0.4985	0.2210	66.1	16,200	3.99
6	0.5037	0.2255	74.5	17,420	4.02
7	0.4957	0.2304	76.7	17,480	4.07
Avg.				17,580	4.02
Std. Dev.				±1,095	±0.045
Temperature 200°F					
1	0.5025	0.2674	77.4	12,930	3.21
2	0.4992	0.2466	48.7	9,630	3.08
3	0.5011	0.2641	81.6	14,010	3.11
4	0.5005	0.2511	69.9	13,290	3.09
5	0.5000	0.2427	55.1	11,220	3.13
6	0.5550	0.2765	46.3	6,610 [2]	2.98
7	0.4972	0.2270	46.3	10,840	3.09
Avg.				11,970	3.10
Std. Dev.				±1,440	±0.05

TABLE V (Concluded)

Spec. No.	Width (in.)	Thickness (in.)	Max. Load (lb.)	Ultimate Flexural Strength (σ_b, psi)	Modulus of Elasticity E_b, psi $\times 10^{-5}$
Temperature 250°F					
1	0.4993	0.2385	28.4	6,000	1.36
2	0.4816	0.2602	26.9	4,950	1.24
3	0.5032	0.2800	25.4	3,860[2]	1.12[2]
4	0.4904	0.2297	23.6	5,470	1.78
5	0.4992	0.2520	30.4	6,830	1.61
6	0.5048	0.2655	22.7	3,830	1.44
7	0.4985	0.2498	21.6	4,170	1.47
Avg.				5,480	1.48
Std. Dev.				±1,040	±0.225
Temperature 300°F					
1	0.5010	0.2610	3.75	660	0.224
2	0.5009	0.2738	4.41	700	0.290
3	0.4966	0.2532	3.97	750	0.298
4	0.5076	0.2457	3.31	650	0.248
5	0.4986	0.2209	3.97	610	0.235
6	0.5031	0.2650	3.31	560	0.249
7	0.5018	0.2364	3.53	760	0.282
Avg.				670	0.261
Std. Dev.				±72.5	±0.0269

[1] Bubble in shank of test specimen caused premature failure.
[2] Some residual internal strains present as indicated by polarized light examination.

TABLE VI

TENSILE PROPERTIES OF EPOXY RESIN AT ELEVATED TEMPERATURES
(6.5 pph TMB in DEBA, Cure Cycle 18 hr. - 180°F, 12 hr. - 350°F)

Spec. No.	Width (in.)	Thickness (in.)	Max. Load (lb.)	Ultimate Tensile Strength (psi)	Tensile Mod. of Elasticity (psi x 10^{-5})	Elongation at Rupture (%)
Temperature 77°F						
1	0.5039	0.2436	900	7,340	5.92	1.40
2	0.5066	0.2475	1,400	11,180	5.36	2.48
3	0.5046	0.2424	1,490	12,300	5.83	2.56
4	0.5064	0.2430	911	7,410	6.21	1.49
5	0.5051	0.2489	1,195	9,520	5.80	2.00
6	0.5035	0.2612	775	5,900[1]	5.52	1.00[1]
7	0.5030	0.2485	1,290	10,300	-	-
Avg.				9,675	5.77	1.99
Std. Dev.				±2,010	±0.363	±0.52
Temperature 150°F						
1	0.5031	0.2459	1,355	10,950	5.05	2.82
2	0.5064	0.2536	1,235	9,620	4.83	2.36
3	0.5035	0.2500	1,408	10,970	4.93	2.72
4	0.5033	0.2469	1,455	11,700	4.70	3.08
5	0.5059	0.2424	915	7,460	4.76	1.57[1]
6	0.5115	0.2516	1,095	9,540	4.85	1.82
7	0.5044	0.2491	882	9,300	4.39	2.06
Avg.				10,180	4.79	2.476
Std. Dev.				±1,144	±0.110	±0.255

TABLE VI (Concluded)

Spec. No.	Width (in.)	Thickness (in.)	Max. Load (lb.)	Ultimate Tensile Strength (psi)	Tensile Mod. of Elasticity (psi x 10^{-5})	Elongation at Rupture (%)
Temperature 200°F						
1	0.5062	0.2537	574	4,400[1]	4.00	1.41[1]
2	0.5064	0.2518	1,035	8,130	3.64	2.56
3	0.5031	0.2416	925	7,600	3.49	2.72
4	0.5056	0.2300	805	6,900	3.63	4.18
5	0.5055	0.2358	745	6,260	3.59	4.82
6	0.5067	0.2560	729	5,610	3.55	2.59
7	0.5010	0.2497	872	6,970	3.16	4.00
Avg.				6,912	3.58	3.478
Std. Dev.				±900.2	±0.798	±0.978
Temperature 250°F						
1	0.5065	0.2410	430	2,210	1.72	2.82
2	0.4950	0.2419	305	2,540	1.95	1.44
3	0.5062	0.2510	254	2,000	1.44	1.78
Avg.				2,250	1.70	2.01

[1] Premature failure caused by extensometer.

TABLE VII

ULTIMATE TENSILE STRENGTH OF EPOXY RESIN AT
ELEVATED TEMPERATURES

Spec. No.	Width (in.)	Thickness (in.)	Max. Load (lb.)	Ultimate Tensile Strength (psi)
Temperature 77°F				
1	0.5023	0.2550	1,720	13,450
2	0.5033	0.2425	1,655	13,600
3	0.5046	0.2424	1,490	12,300
4	0.5012	0.2425	1,650	13,550
5	0.5023	0.2510	1,580	12,550
Avg.				13,090
Std. Dev.				±860
Temperature 150°F				
1	0.5057	0.2651	1,655	12,380
2	0.5035	0.2622	1,545	11,710
3	0.5005	0.2512	1,520	12,100
4	0.5002	0.2518	1,310	10,400
5	0.5044	0.2491	1,390	11,050
Avg.				11,550
Std. Dev.				±710
Temperature 200°F				
1	0.4987	0.2466	960	7,900
2	0.4996	0.2619	795	6,100
3	0.5002	0.2518	880	7,000
4	0.5010	0.2497	882	7,050
5	0.5056	0.2300	815	7,000
Avg.				7,010
Std. Dev.				±670

TABLE VII (Concluded)

Spec. No.	Width (in.)	Thickness (in.)	Max. Load (lb.)	Ultimate Tensile Strength (psi)
Temperature 250°F				
1	0.5003	0.2565	615	4,810
2	0.5006	0.2504	615	4,860
3	0.5100	0.2484	685	5,400
4	0.5102	0.2424	610	4,930
5	0.5000	0.2438	585	4,800
Avg.				4,980
Std. Dev.				±800
Temperature 280°F				
1	0.4981	0.2754	231	1,710
2	0.5012	0.2415	88	695
3	0.4992	0.2524	231	1,840
4	0.4989	0.2490	120	970
Avg.				1,300
Std. Dev.				±560
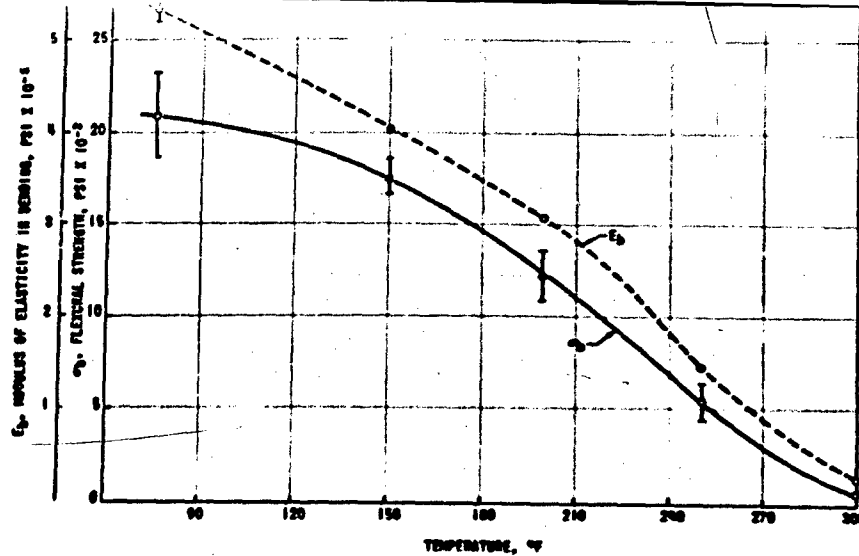
Fig. 14 - Flexural Properties of 6.5 pph TMB Cured
DEBA at Elevated Temperatures
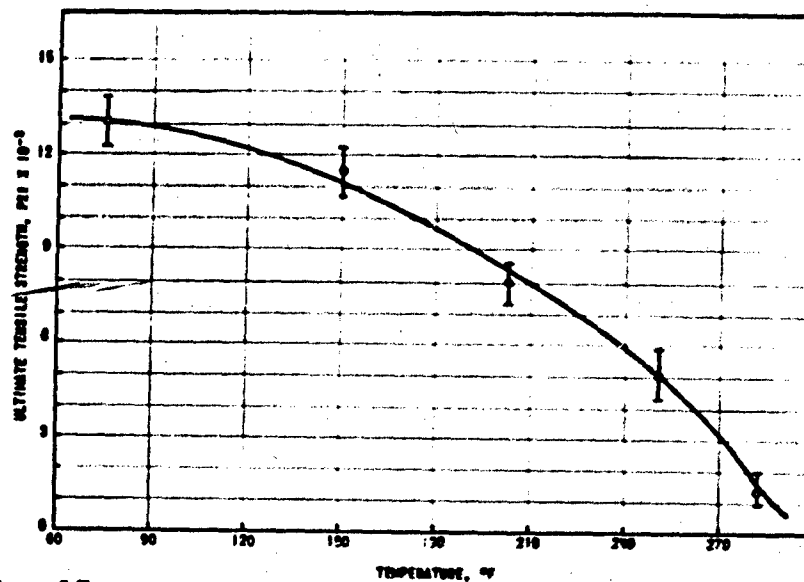
Fig. 15 - Tensile Properties of 6.5 pph TMB Cured
DEBA at Elevated Temperatures
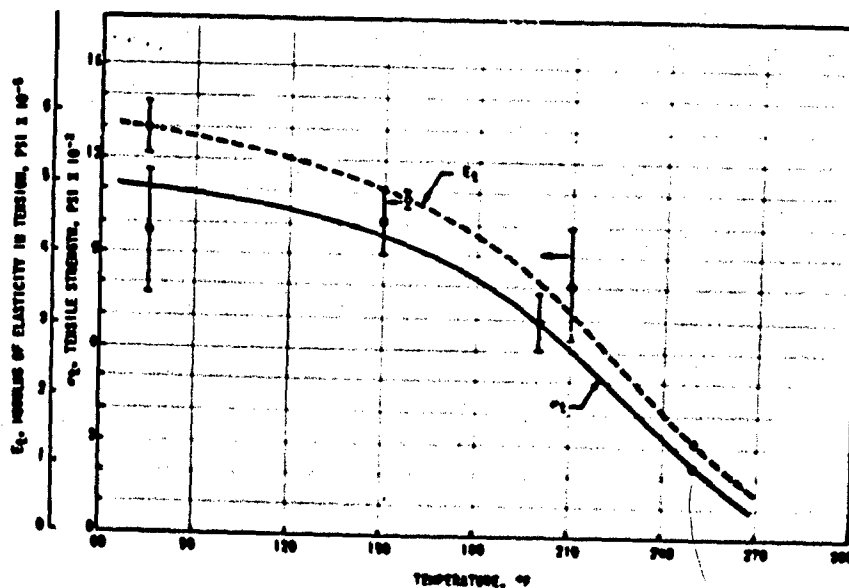
Fig. 16 - Ultimate Tensile Strength of 6.5 pph TMB
Cured DEBA Resin at Elevated Temperatures

Mixtures of 90, 80 and 60 per cent by weight of DEBA and the epoxy novolak were prepared. Trimethoxyboroxine was added to the resin mixtures at the 5 pph level and 6 in. by 6 in. by 1/4 in. plates were cast and cured for 18 hr. at 185°F. The plates were cut into three 2 in. by 6 in. sections and one each cured for 4 hr. at 300°F and 400°F. The flexural modulus of these samples at elevated temperatures was determined on 0.5 in. by 6.0 in. specimens using the technique previously discussed. The results of this experiment are shown in Figs. 17, 18, and 19.

3. Anhydride Cured Saturated Cyclic Epoxide

Vinylcyclohexene dioxide was investigated briefly during the work carried out under Contract NOas 59-6137-c, "Development of High-Temperature Resistant Transparent Plastics", M.R.I. Project 2289-C. The work at that time was based on in situ casting of the resin directly against the hot-stretched acrylic sheet. It was found that vinylcyclohexene dioxide severely swelled the acrylic sheet. Further work with this diepoxide monomer was abandoned at that time.

The change in emphasis, created by the three layer composite, has made further investigation of this monomer desirable. Vinylcyclohexene dioxide yields resins of much higher heat distortion temperatures (with anhydrides) than the bisphenol A epoxide resins.

a. Determination of optimum anhydride content by weight loss on exposure to elevated temperatures: Vinylcyclohexene dioxide is much more sensitive to acid catalysis than bisphenol A epoxides. The initial investigation of this monomer was made with hexahydrophthalic anhydride and endomethylenetetrahydrophthalic anhydride as the co-reactants. Because vinylcyclohexene dioxide is sensitive to acid catalysis, it was necessary to determine an optimum ratio of anhydride to epoxide. Acid catalysis causes some of the epoxide to polymerize through the etherification reaction, thus reducing the amount of epoxide remaining to react with the anhydride.

Determination of the effect of anhydride epoxide ratio on thermal stability has been a satisfactory method for determining the optimum ratio. Ten-gram amounts of 13 different anhydride-epoxide mixtures of mol ratios from 0.3 to 1.2 mol anhydride per mol epoxide, were prepared from hexahydrophthalic anhydride and endomethylenetetrahydrophthalic anhydride with vinylcyclohexene dioxide. One-half of one per cent, by weight, of a 60 per cent aqueous solution of benzyltrimethylammonium chloride was added to each mixture. The mixtures were cast into 2.0 cm. glass vials and cured. The hexahydrophthalic (HHPA) vinylcyclohexene dioxide mixtures were cured for 14 hr. at 180°F and 8 hr. at 300°F. The endomethylenetetrahydrophthalic anhydride mixtures were cured at 180°F for 12-1/2 hr. and at 300°F for 18 hr.
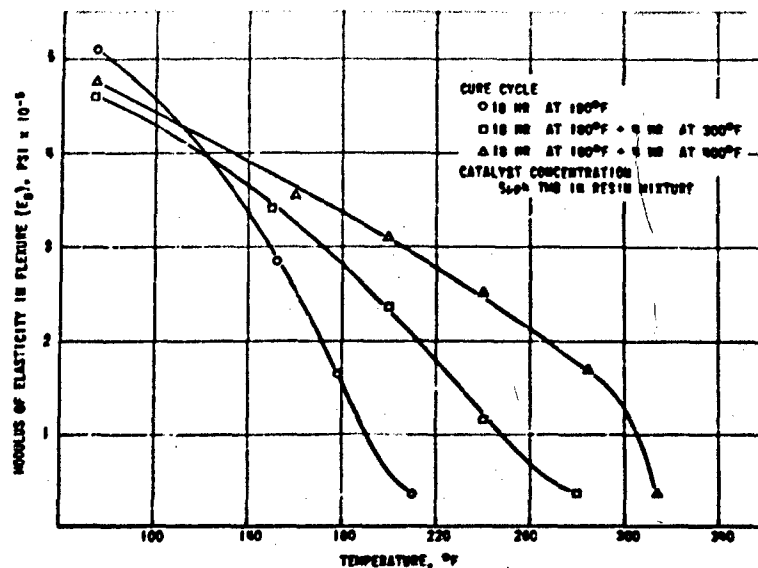
Fig. 17 - Thermal Resistance of Cured 90 Per Cent DEBA
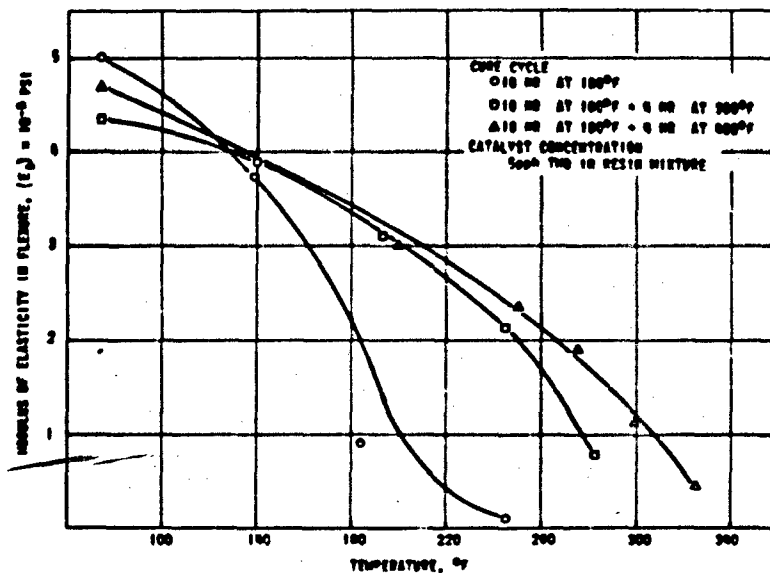10 Per Cent Novolak Resin Mixture

Fig. 18 - Thermal Resistance of Cured 80 Per Cent DEBA
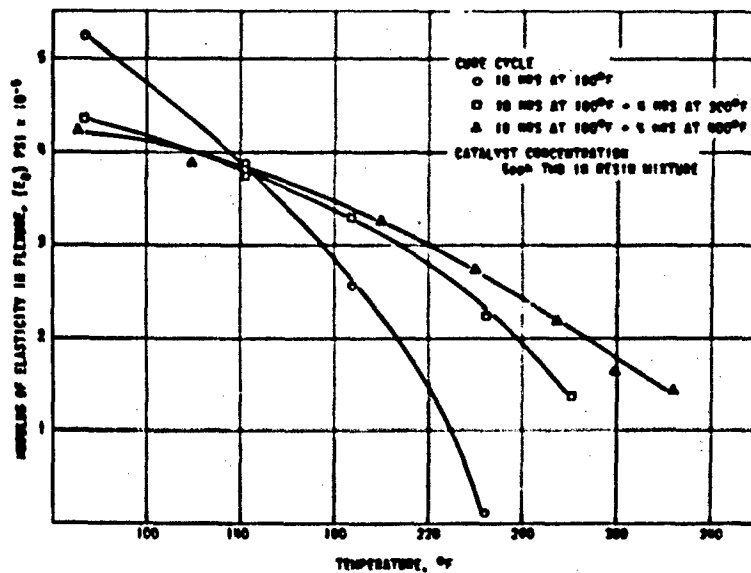20 Per Cent Novolak Resin Mixture

Fig. 19 - Thermal Resistance of Cured 60 Per Cent DEBA
40 Per Cent Novolak Resin Mixture

After the resin mixtures were cured they were cut into test specimens, weighed, and placed in an air-circulating oven at 500°F. The samples were removed from the oven, cooled in a desiccator and reweighed after 4, 8, 17, and 32 hr. of accumulated exposure. The results of this experiment are shown in Figs. 20 and 21; the weight loss after exposure is plotted against the resin composition.

b. Resins from vinylcyclohexene dioxide: The optimum ratio of epoxide to anhydride for vinylcyclohexene dioxide was 0.5 to 0.6 mol hexahydrophthalic anhydride per mol epoxide and 0.45 to 0.50 for the endomethylenetetrahydrophthalic anhydride. These ratios yielded resins with the smallest weight loss after exposure to 500°F. The endomethylenetetrahydrophthalic anhydride resin was more stable than the hexahydrophthalic anhydride, exhibiting a weight loss of only 3.6 per cent after 32 hr. of exposure at 500°F.

Cast sheets of the anhydride cured vinylcyclohexene dioxide were prepared. The 6 x 6 x 1/4 in. sheets were cast between poly(vinyl alcohol)-coated ferro-type plates. Specimens with the following compositions were prepared:

1. Vinylcyclohexene dioxide   1.0 mol
    Hexahydrophthalic anhydride   1.0 mol
    Benzyltrimethylammonium chloride
        (60 per cent solution in water)   0.25 weight per cent of
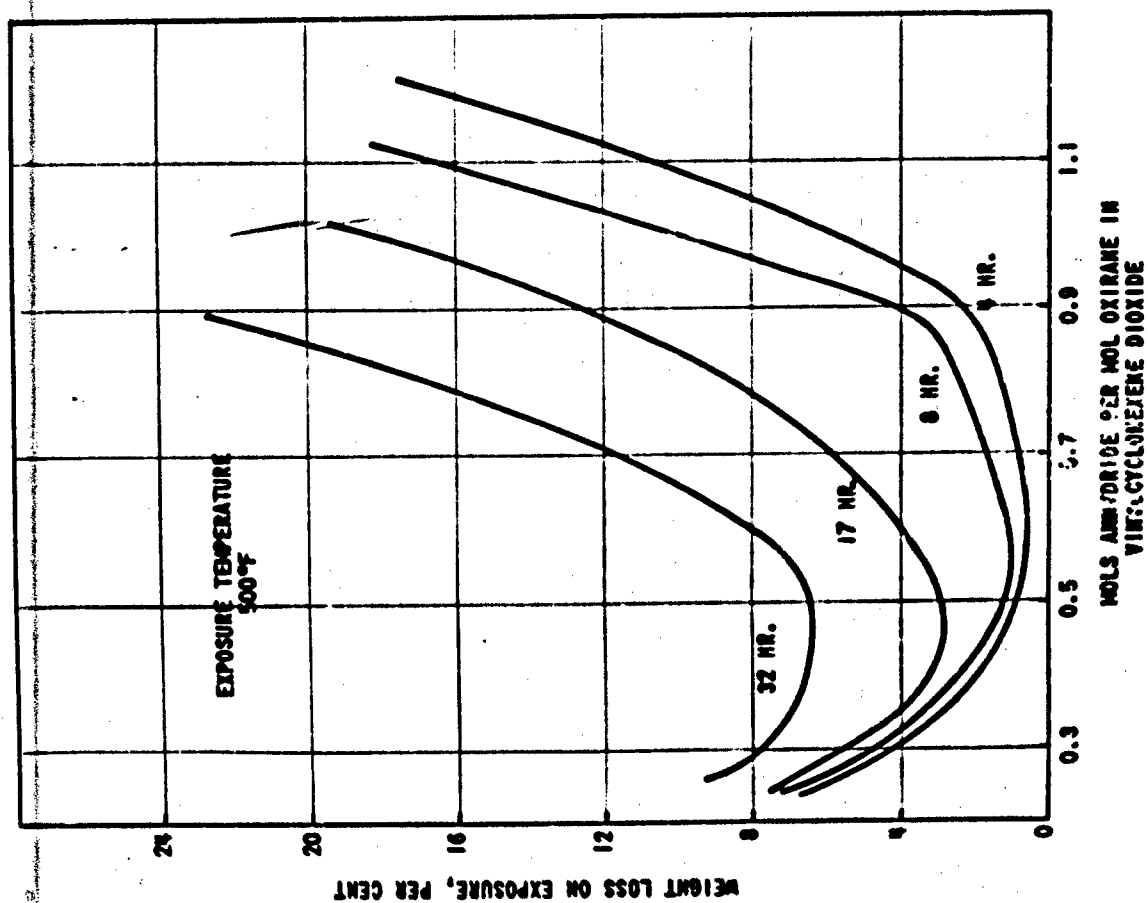   resin mixture

2. Vinylcyclohexene dioxide   1.0 mol
    Endomethylenetetrahydrophthalic
        anhydride   1.0 mol
    Benzyltrimethylammonium chloride
        (60 per cent solution in water)   0.25 weight per cent of
                                                            resin mixture

3. Vinylcyclohexene dioxide   1.0 mol
    Endomethylenehexahydrophthalic
        anhydride   1.0 mol
    Benzyltrimethylammonium chloride
        (60 per cent solution in water)   0.25 weight per cent in
                                                            resin mixture

4. Diglycidyl ether of bisphenol A   1.0 mol
    Hexahydrophthalic anhydride   1.8 mols
    Benzyltrimethylammonium chloride
        (60 per cent solution in water)   0.50 weight per cent in
                                                            resin mixture
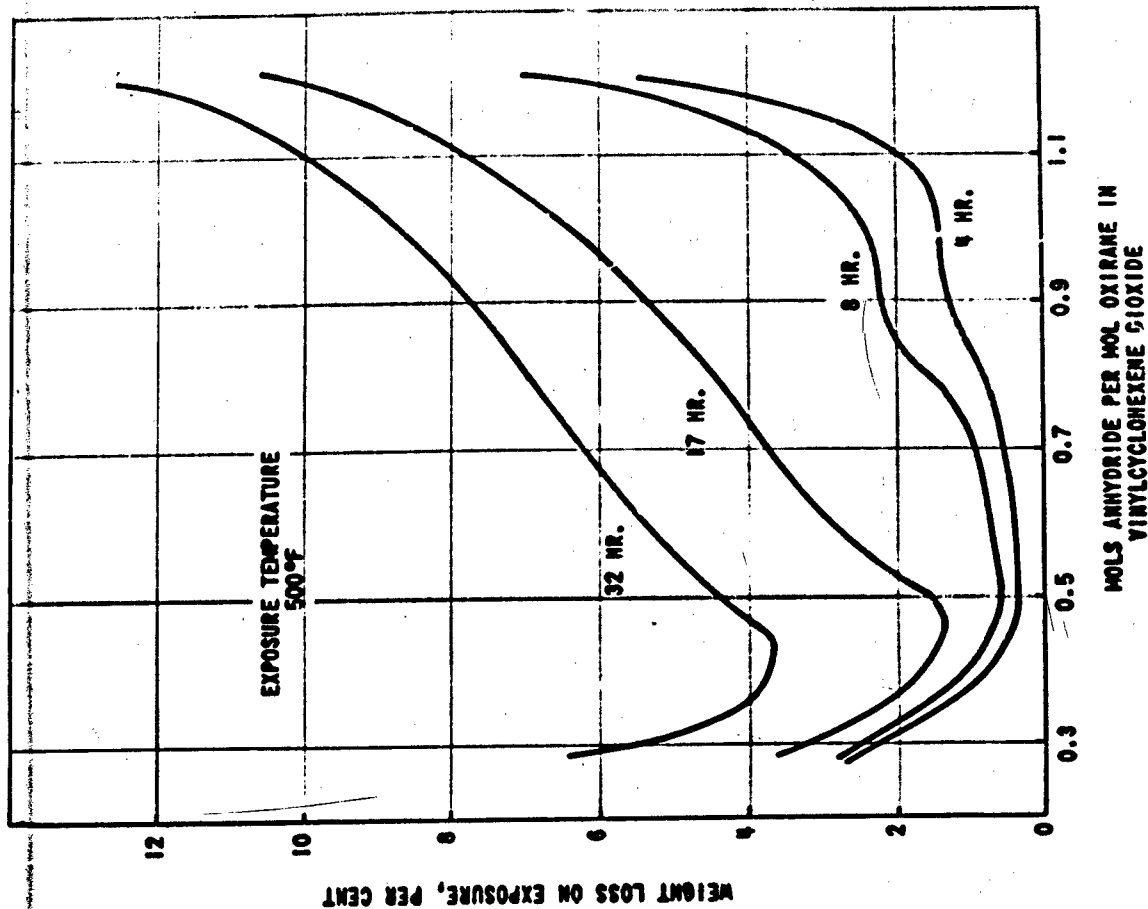
Fig. 21 - Effect of Anhydride/Epoxide Ratio on Thermal
Stability of Vinylcyclohexene Dioxide-Endo-
methylenetetrahydrophthalic Anhydride Resin

Fig. 20 - Effect of Anhydride/Epoxide Ratio on Thermal
Stability of Vinylcyclohexene Dioxide-
Hexahydrophthalic Anhydride Resin

5.	Diglycidyl ether of bisphenol A	1.0 mol
	Endomethylenehexahydrophthalic anhydride	1.8 mols
	Benzyltrimethylammonium chloride (60 per cent solution in water)	0.50 weight per cent in resin solution
6.	Diglycidyl ether of bisphenol A	1.0 mol
	Endomethylenetetrahydrophthalic anhydride	1.8 mols
	Benzyltrimethylammonium chloride (60 per cent solution in water)	0.50 weight per cent in resin solution

The endomethylenetetrahydrophthalic anhydride (bicyclo[2.2.1]hept-5-ene-2,3,-dicarboxylic anhydride) was the commercial product distilled at 2.0 mm. Hg, b.p. 130-4°F. The endomethylenehexahydrophthalic anhydride was made by low pressure hydrogenation of the tetrahydro anhydride with Adams catalyst.[1] The hydrogenated product was distilled at 2.0 mm. Hg, b.p. 148-152°F. The hexahydrophthalic anhydride, vinylcyclohexene dioxide and diglycidyl ether of bisphenol A were commercial products used as received.

All castings were cured for 18 hr. at 150°F, and 3 hr. at 250°F. Samples containing the endomethylene anhydrides were given an additional 3 hr. at 350°F. Flexural test specimens, 6 x 1/2 x 1/4 in., were cut from each plate. The modulus of elasticity in bending (E_b) of these samples was determined at elevated temperatures. The results of these tests are shown in Figs. 22, 23, and 24.

c. Color stability of vinylcyclohexene dioxide resins at elevated temperatures: The heat resistance of hexahydrophthalic anhydride and endomethylenehexahydrophthalic anhydride resins was considerably superior to the TMB-cured DEBA. It was expected that the resistance to discoloration should also be superior. Two-inch square pieces of the various vinylcyclohexene dioxide resins were subjected to cycling exposures of 10, 20, and 40 min. at 410°F. The light transmission of the specimens was measured after each exposure period. Specimens were placed in an air-circulating oven at 410°F for the time period indicated. After cure, they were removed and allowed to cool for 15 min. The light transmission was then determined and the specimens returned to the oven for the next cycle. The results of these experiments are shown in Figs. 25 and 26.

---

[1] Final Report, Contract NOas-59-6137-c, "Development of High-Temperature Resistant Transparent Plastics", January 20, 1960, Midwest Research Institute, Kansas City, Missouri.
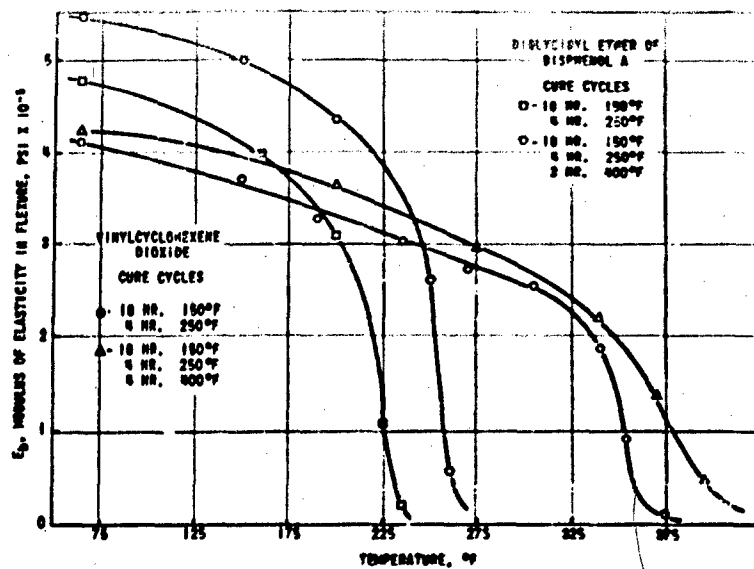
Fig. 22 - Flexural Modulus of Hexahydrophthalic Anhydride
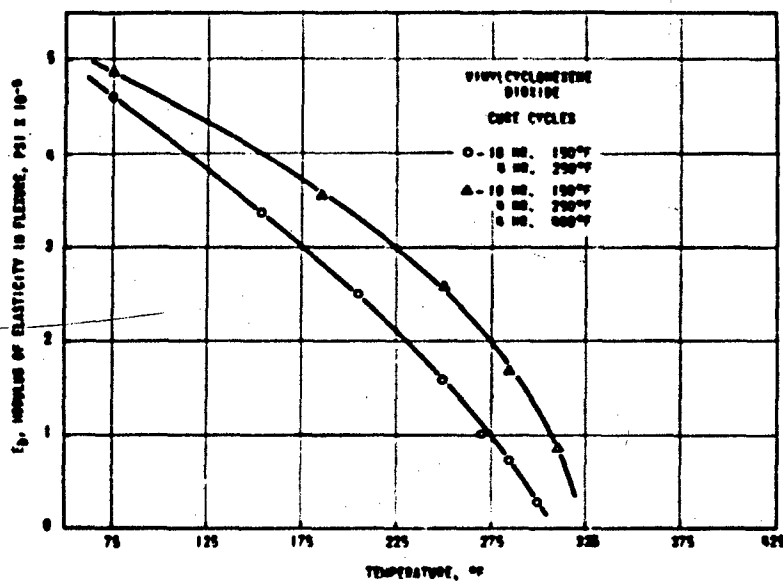Cured Epoxide Resins at Elevated Temperatures

Fig. 23 - Flexural Modulus of Endomethylenetetrahydrophthalic
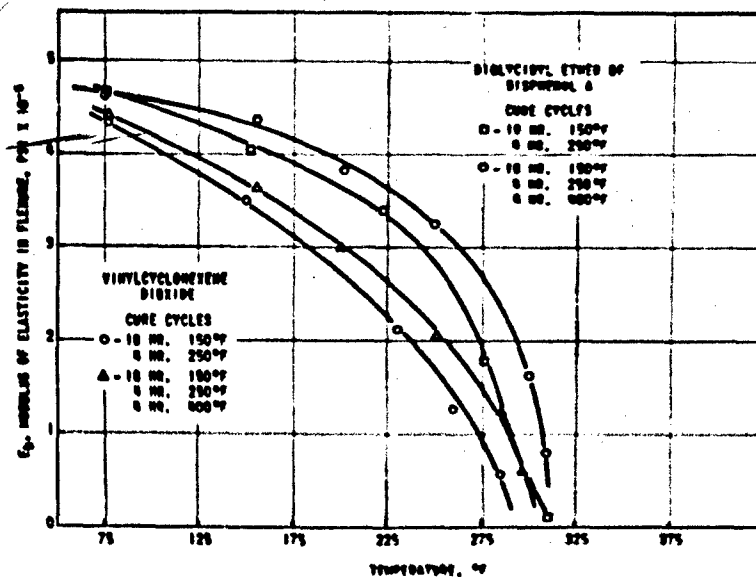Anhydride Cured Resin at Elevated Temperatures

Fig. 24 - Flexural Modulus of Endomethylenehexahydrophthalic Anhydride
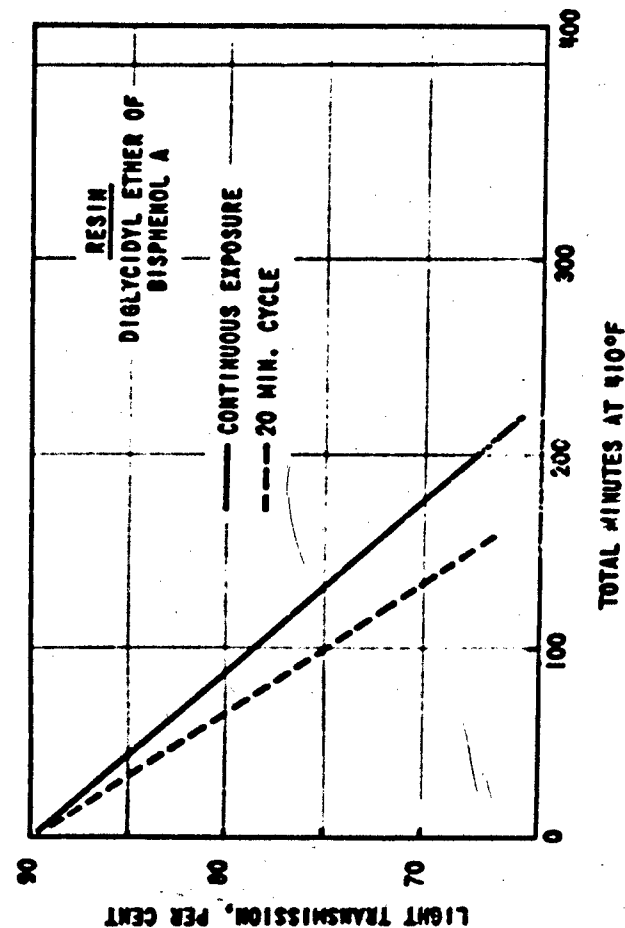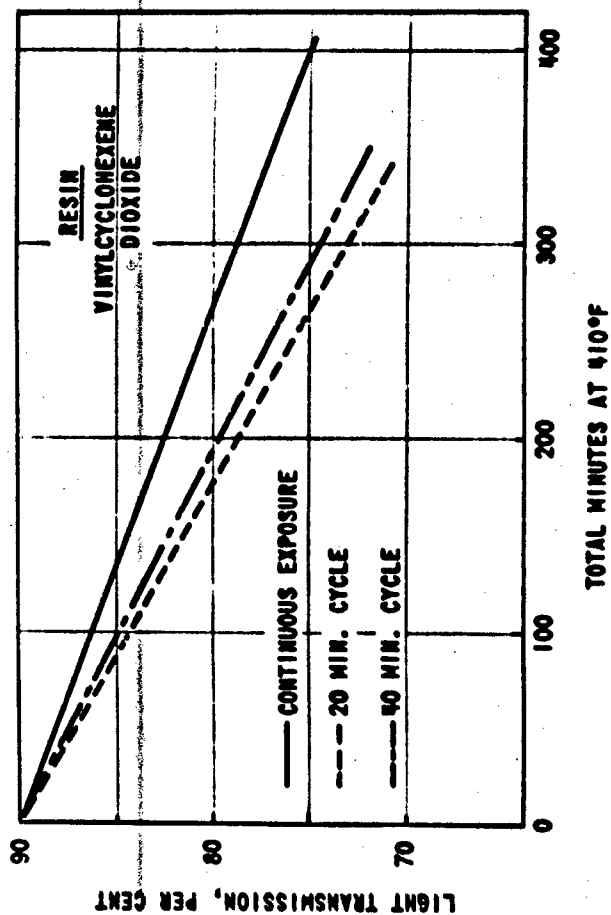Cured Epoxide Resins at Elevated Temperatures

Fig. 25 - Color Stability of Hexahydrophthalic
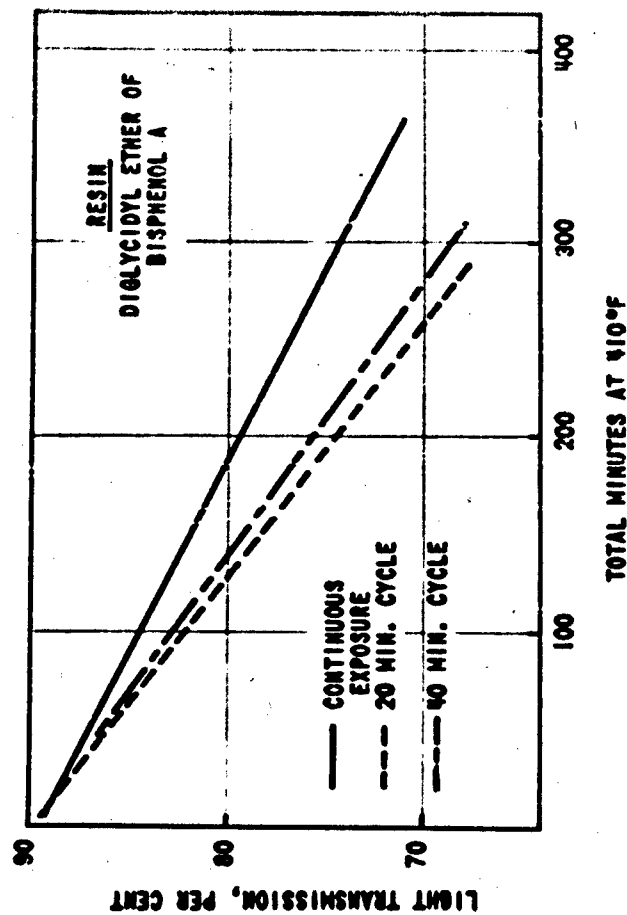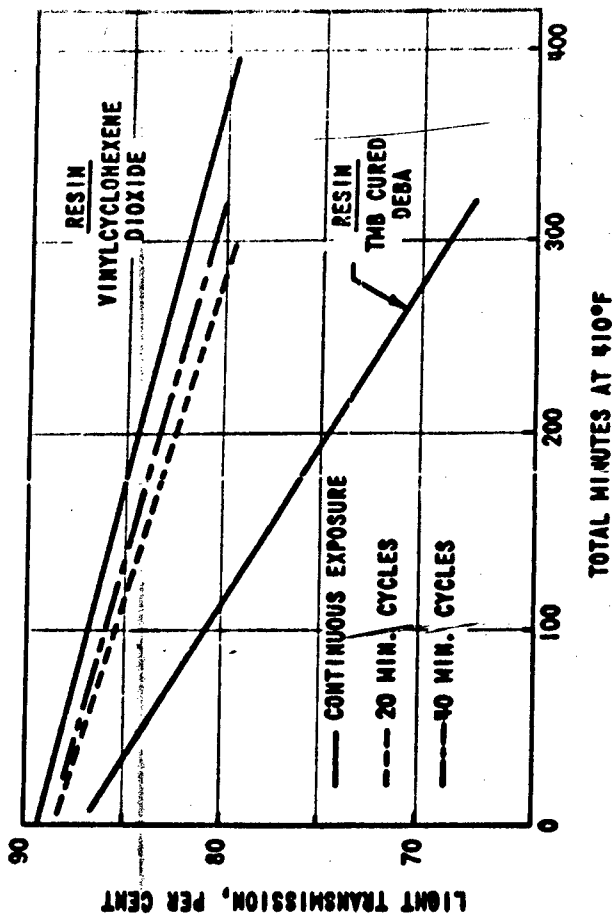Anhydride Cured Epoxide

Fig. 26 - Color Stability of Endomethylenehexa-
hydrophthalic Anhydride Cured Epoxide

d. Optimization of anhydride - vinylcyclohexene dioxide ratios to obtain maximum thermal rigidity:

(1) Hexahydrophthalic anhydride: Previous work with resins obtained from hexahydrophthalic anhydride (HHPA) and vinylcyclohexene dioxide (VCHDO) yielded cured resins with good color stability and resistance to temperatures approaching 400°F. There was, however, some doubt that the optimum anhydride-to-resin ratio, as determined by weight loss, would produce the most rigid resin. The following section outlines work done toward optimizing the anhydride-to-resin ratio and determination of the amount of catalyst required.

Mixtures of vinylcyclohexene dioxide and hexahydrophthalic anhydride per mol equivalent epoxide were catalyzed with 0.25 pph of a 60 per cent aqueous solution of benzyltrimethylammonium chloride. These mixtures were cast into 6-in. by 6-in. by 0.25-in. sheets. The castings were initially cured at 180°F until gelation occurred (about 4 hr.) and then 2 hr. at 240°F.

The plate glass molds used were coated with the carboxymethyl-cellulose poly(vinyl alcohol) release agent. After the initial cure period was completed, the molds were slowly cooled in the curing oven. As the molds cooled, the cured castings released from the mold surfaces quite readily. The molds must be cooled slowly to prevent thermal shock and resulting fracture of the glass.

The cured sheets were cut into 6-in. by 0.5-in. strips for determination of flexural properties. The flexural test specimens were then subjected to additional curing at increasing temperatures up to 450°F. Samples were withdrawn for testing as shown in Figs. 27, 28, and 29. The results of these tests are shown in these figures. The modulus of elasticity in bending (E_b) is plotted against temperature in Figs. 27 and 28. Figure 29 shows the effect of mixture ratios on the temperature at which the E_b is equal to 2 x 10^5 and 10^5 psi.

The optimum ratio of hexahydrophthalic anhydride to vinylcyclohexene dioxide was 0.7 mol anhydride per mol epoxide equivalent. Three sets of 6 x 6 x 0.25-in. plates of a mixture of 0.7 mol anhydride per 0.5 mol (1 equivalent mol) vinylcyclohexene dioxide catalyzed with 0.15, 0.30 and 0.60 pph of the 60 per cent aqueous solution of benzyltrimethylammonium chloride (0.09, 0.18, and 0.36 pph active catalyst) were cast and cured. After the 240°F curing period was complete, flexural test specimens were prepared and subjected to additional cure at 350, 400, and 450°F for 2 hr. at each tempera-
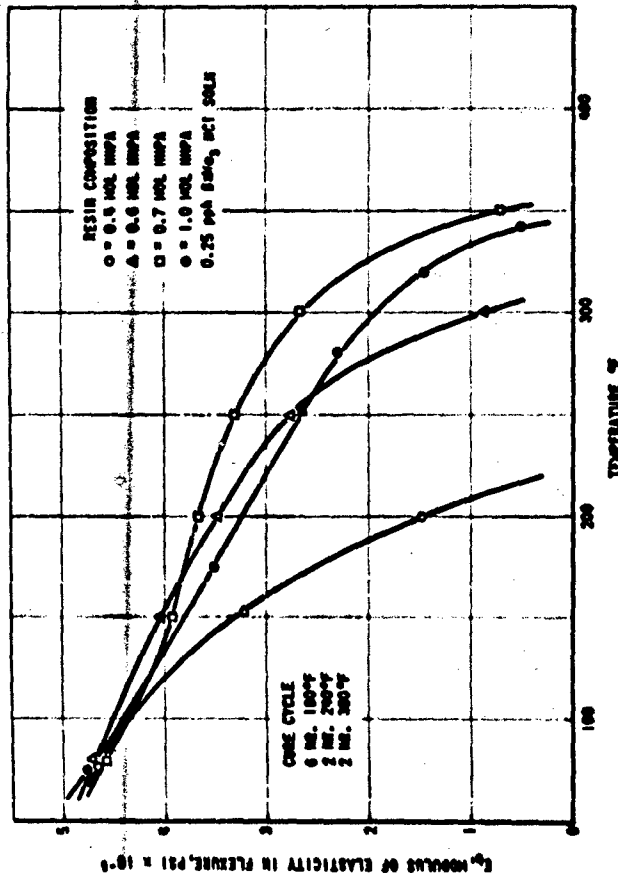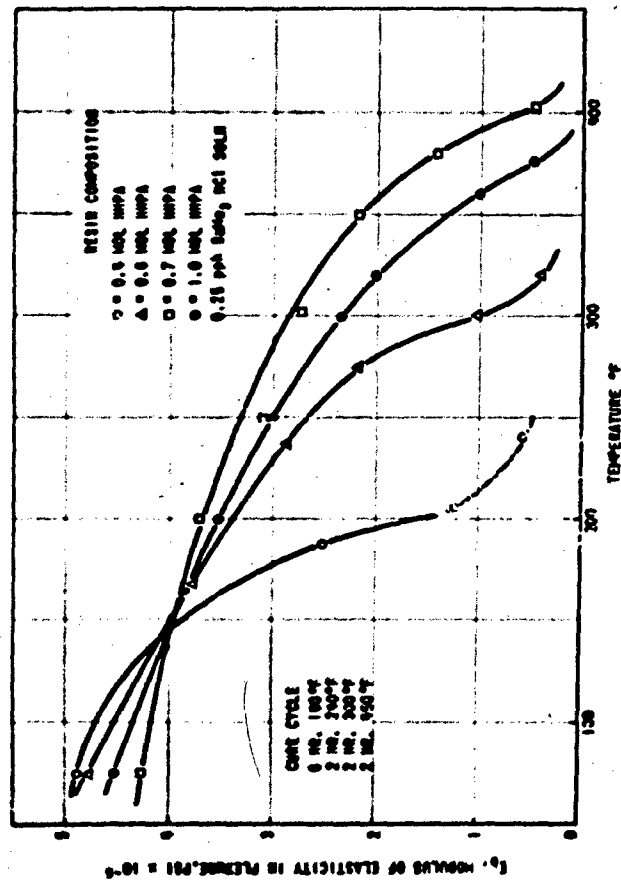
Fig. 29 - Optimum Ratios for HHPA - VCHDO Resins

Fig. 27 - E_b for Resins of Varying HHPA - VCHDO Ratios (300°F Cure)

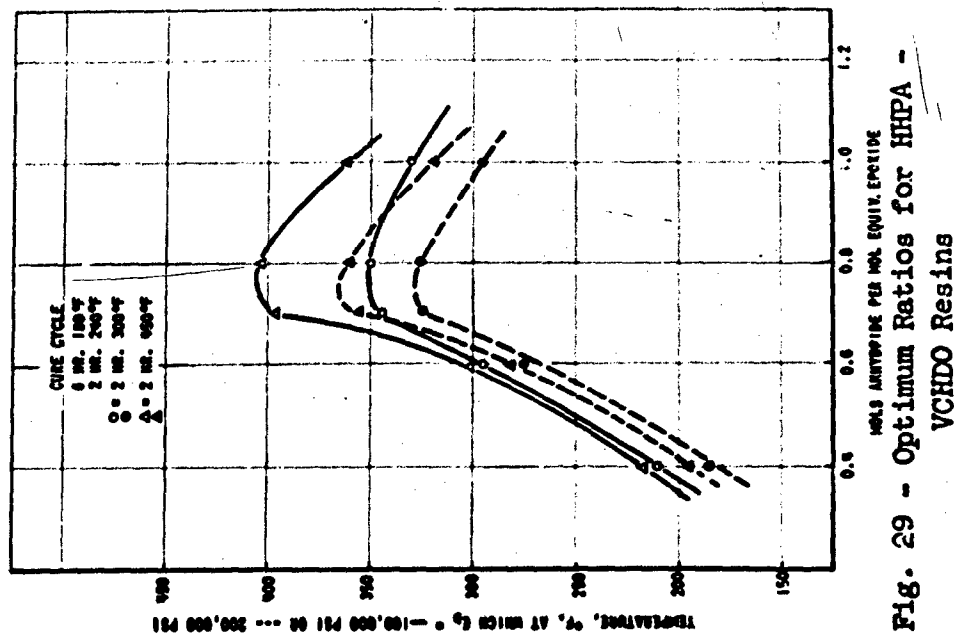Fig. 28 - E_b for Resins of Varying HHPA - VCHDO Ratios (450°F Cure)

ture. Samples were withdrawn for testing at the end of each period. The results of these tests are shown in Figs. 30, 31 and 32.

(2) **Endomethylenetetrahydrophthalic anhydride (EMTHPA)**: The initial work with this anhydride was somewhat disappointing as the resins obtained did not have good thermal resistance. A series of experiments to determine the optimum anhydride - VCHDO ratio were carried out. Sheets of the resins made with ratios of 0.4 to 1.1 mol anhydride per mol equivalent epoxide were cast and cured as outlined in the previous section. The samples were cured at 300°F, 450°F, and 550°F for 2-hr. periods. The results from these tests are shown in Figs. 33, 34, 35, and 36. The temperature at which the flexural modulus (E_b) is equal to 2 x 10^5 psi and 10^5 psi is plotted against composition in Fig. 36, which shows the maximum rigidity to fall between 0.70 and 0.75 mol anhydride per mol equivalent VCHDO.

The effect of catalyst concentration on the resin thermal resistance is shown in Figs. 37, 38, and 39. The procedure for obtaining these data was the same as used with the hexahydrophthalic anhydride, except that the curing temperatures were higher.

The higher curing temperatures created considerable discoloration of this resin system, especially at 550°F where the castings turned black. The initial discoloration was high. This anhydride does not produce a colorless cured system and was examined only because of its similarity to the endomethylenehexahydrophthalic anhydride and its availability. The endomethylenehexahydrophthalic anhydride must be prepared in the laboratory and is thus not readily available in large quantity.

(3) **Endomethylenehexahydrophthalic anhydride**: Resins obtained from vinylcyclohexene dioxide and endomethylenehexahydrophthalic anhydride (EMHHPA) were the most resistant to discoloration at 400°F of all the resins investigated to date. The limited availability of this anhydride reduced somewhat the number of tests that could be performed. Mixtures of 0.55, 0.65, and 0.80 mol anhydride per mol equivalent of vinylcyclohexene dioxide. were catalyzed with 0.25 pph benzyltrimethylammonium chloride and cured using temperatures up to 550°F. The flexural moduli at elevated temperatures were determined and are shown in Figs. 40, 41, and 42.

These castings had a light pink color after the initial cure cycle at 240°F. These castings did not gain much additional color at 450°F. At 550°F considerable surface oxidation occurred.
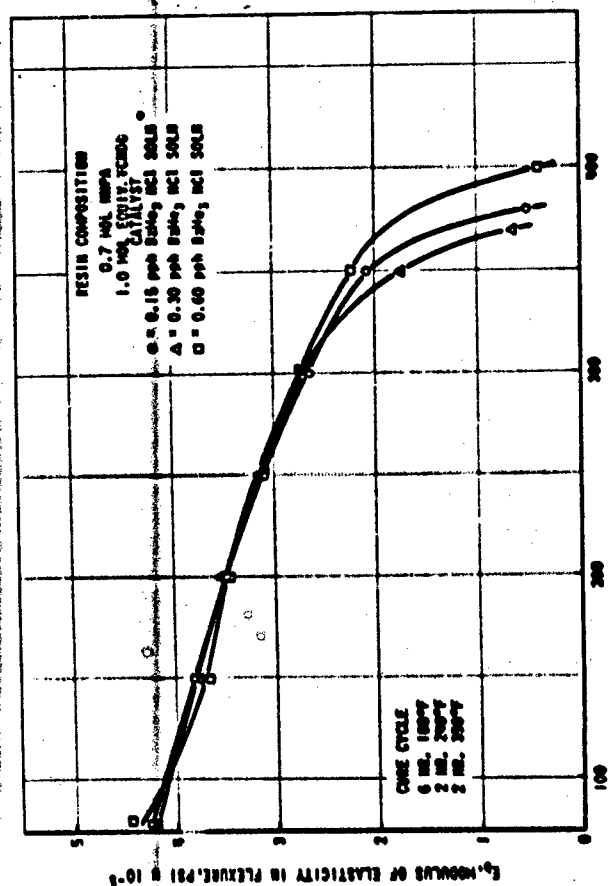
Fig. 32 - Effect of Catalyst Concentrations on Thermal
Rigidity of HHPA - VCHDO Resins

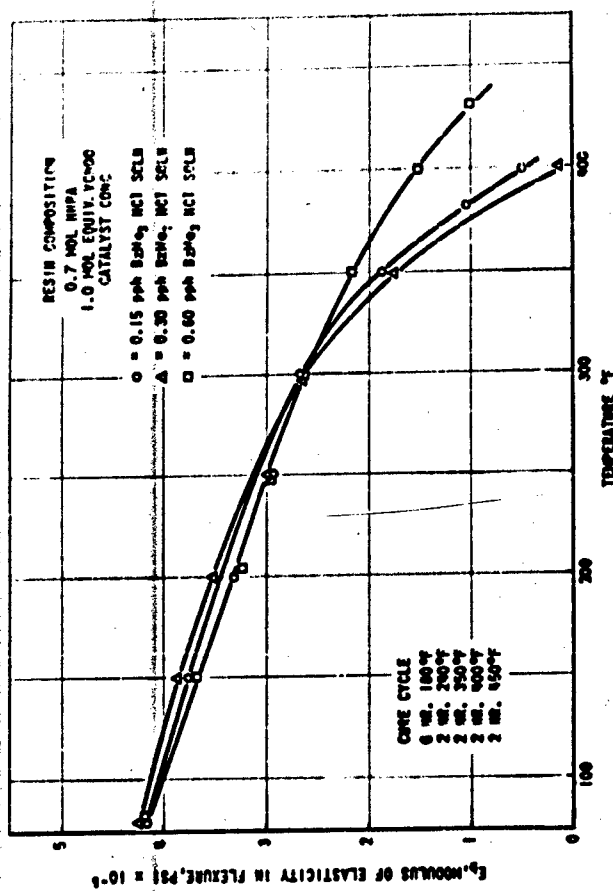Fig. 33 - E_b for Resins of Various EMTHPA - VCHDO
Ratios (300°F Cure)

Fig. 30 - Effect of Catalyst Concentration on Thermal
Rigidity of HHPA - VCHDO Resins

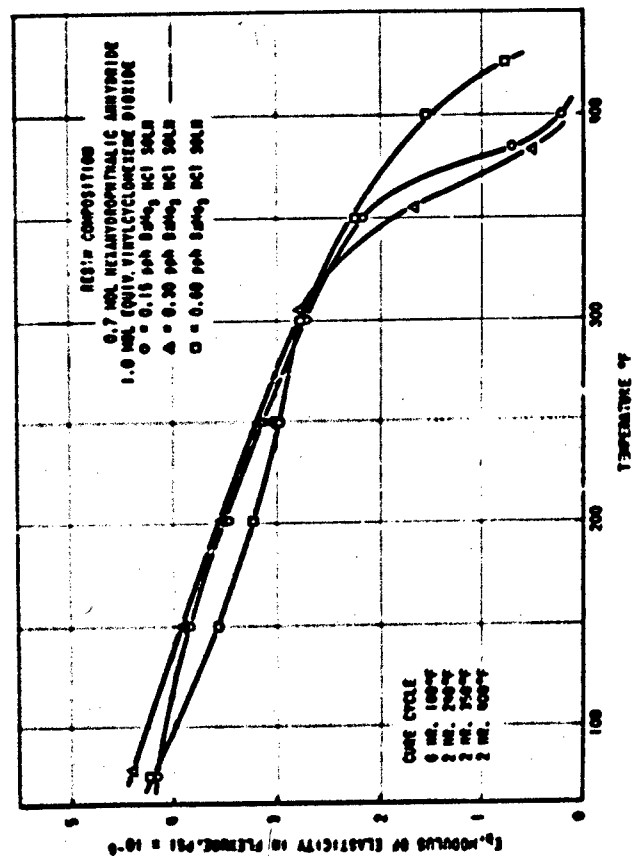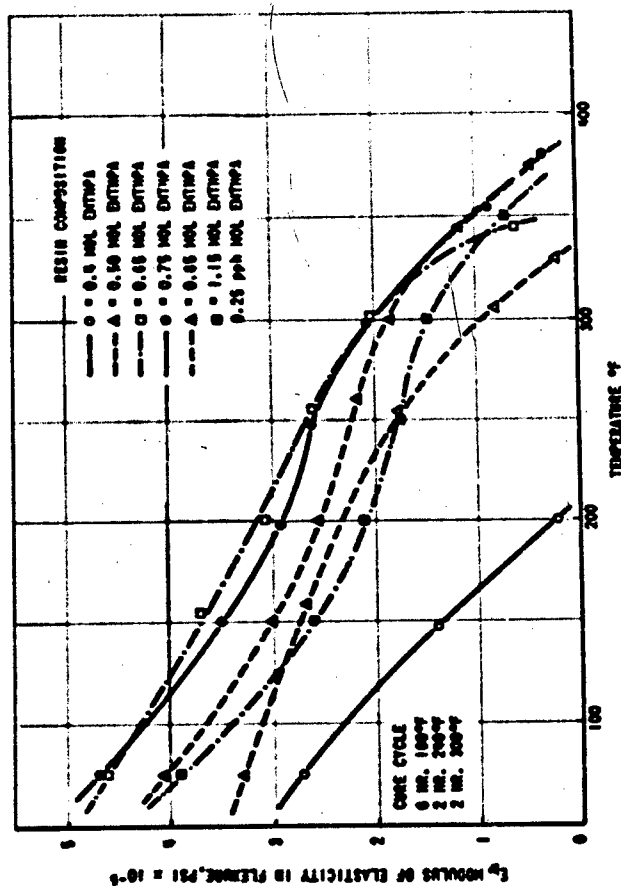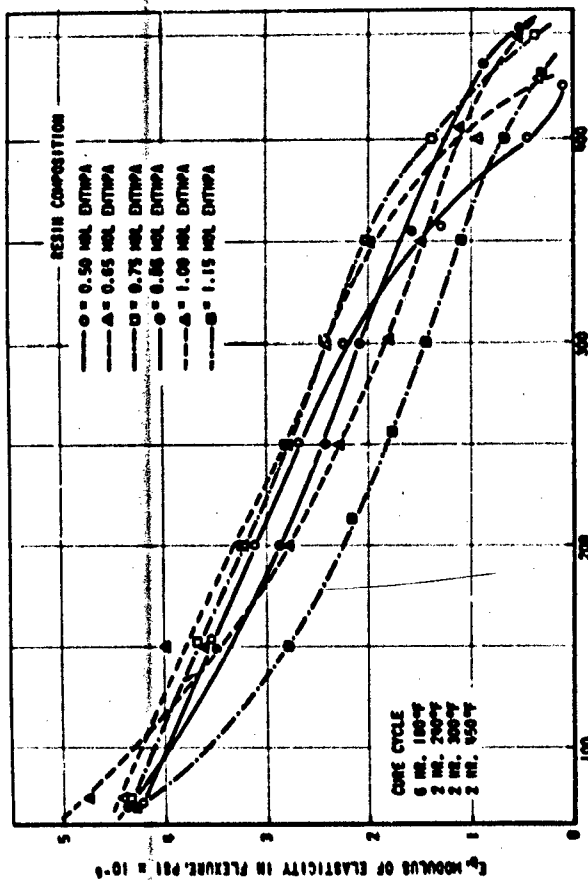Fig. 31 - Effect of Catalyst Concentration on Thermal
Rigidity of HHPA - VCHDO Resins

- 44 -
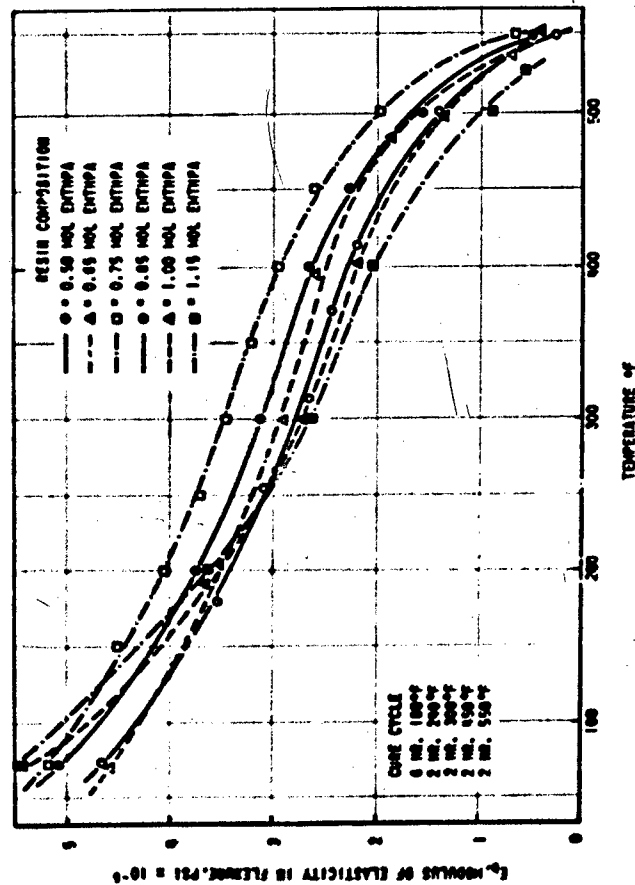
Fig. 36 - Optimization of EMTHPA - VCHDO Ratio

Fig. 34 - E_b for Resins of Various EMTHPA - VCHDO Ratios (450°F Cure)

Fig. 35 - E_b for Resins of Various EMTHPA - VCHDO Ratios (550°F Cure)

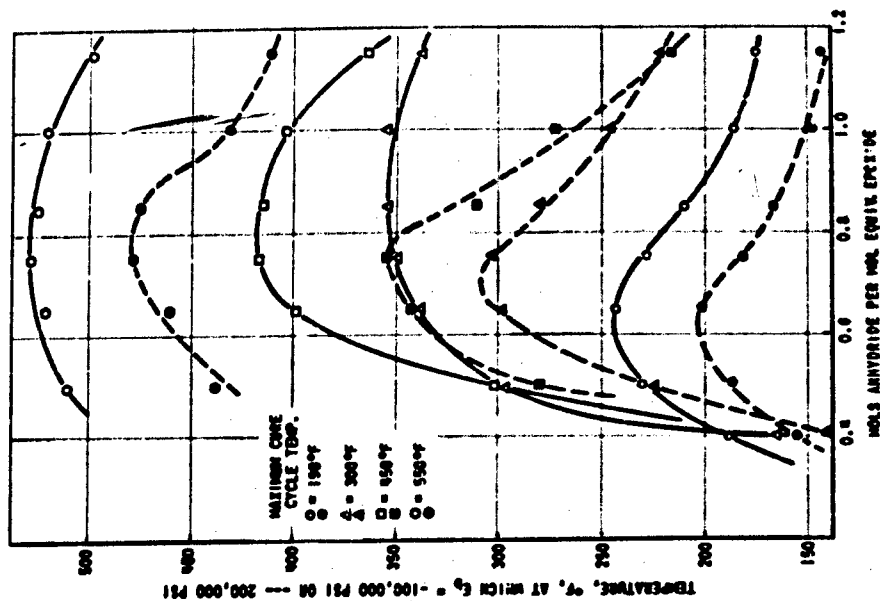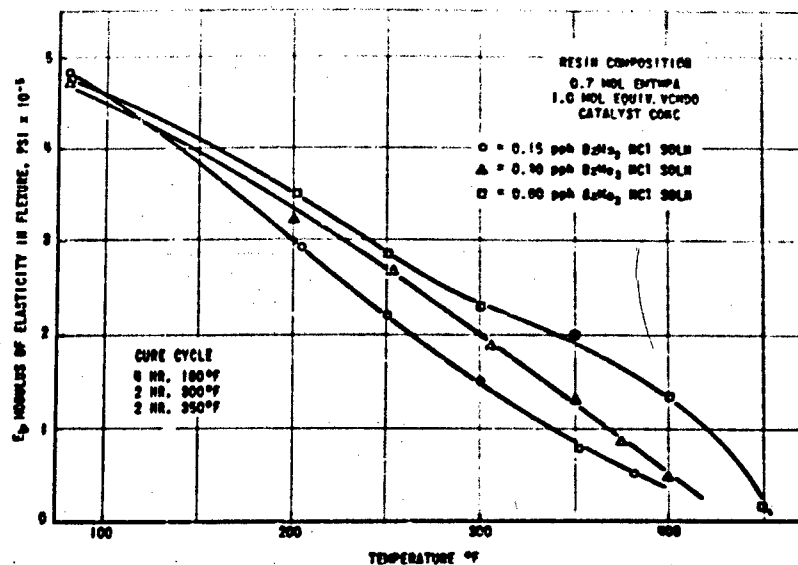Fig. 37 - Effect of Catalyst Concentration on
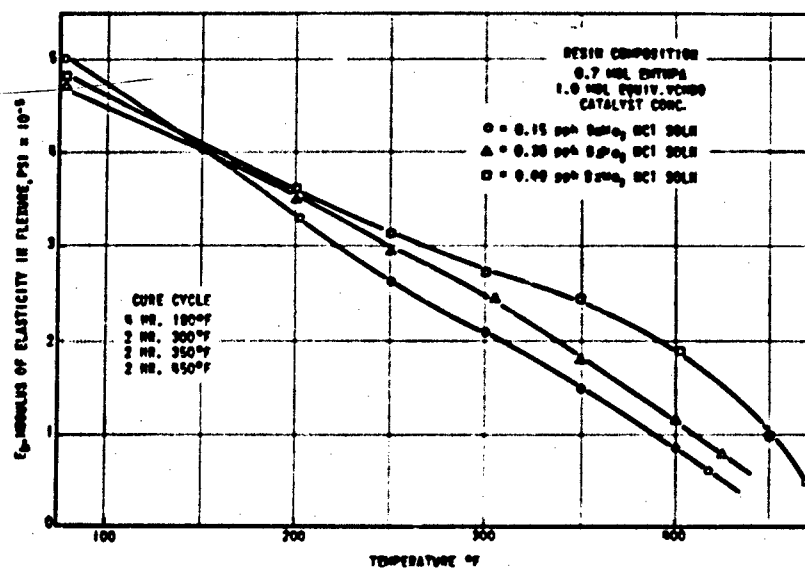EMTHPA - VCHDO Resins (350°F Cure)

Fig. 38 - Effect of Catalyst Concentration on
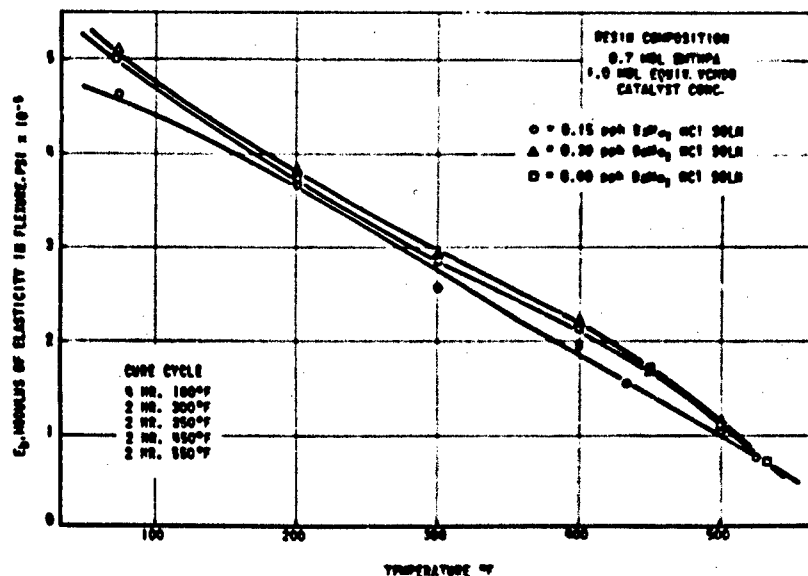EMTHPA - VCHDO Resins (450°F Cure)

Fig. 39 - Effect of Catalyst Concentration on
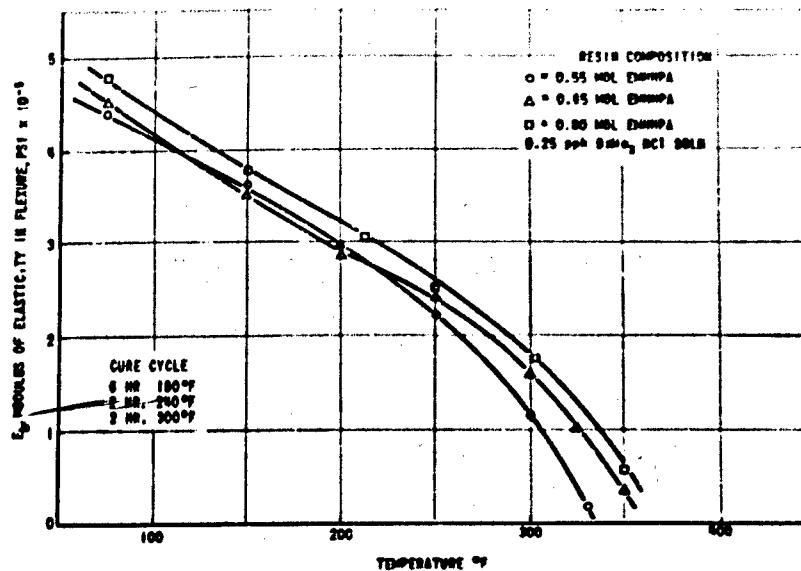EMTHPA - VCHDO Resins (550°F Cure)

Fig. 40 - E_b for Resins of Various EMHHPA - VCHDO Ratios (300°F Cure)
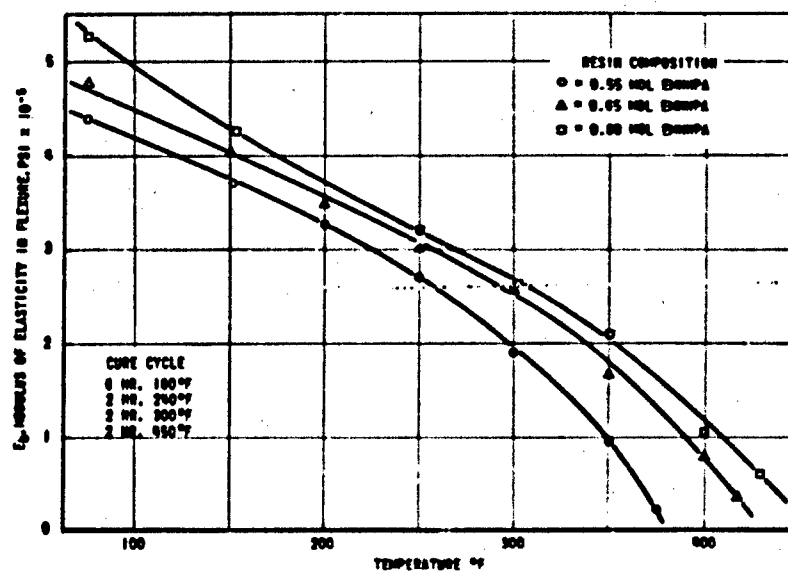

Fig. 41 - E_b for Resins of Various EMHHPA - VCHDO Ratios (450°F Cure)
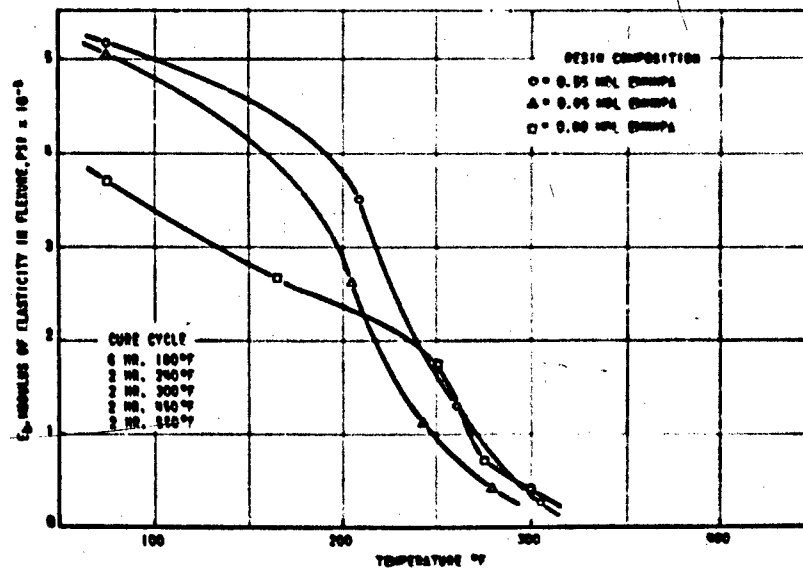

Fig. 42 - E_b for Resins of Various EMHHPA - VCHDO Ratios (550°F Cure)

(4) <u>Development of a film-forming release agent for glass</u>:
The procedures used for preparing the laboratory sheet samples of the thermoset resins have not produced optically acceptable castings. The castings were not consistent either in thickness or in surface smoothness. It was apparent that polished glass surfaces would be required to produce the desired surfaces. A number of mold-release agents including silicones, fluorinated waxes, modified natural and synthetic waxes, organic solvent-soluble film formers and water-soluble film-forming resins were investigated.

Several formulations of water-soluble, film-forming, mold release agents were investigated. One of these proved to be effective. Outlined below is the formulation of the carboxymethylcellulose poly(vinyl alcohol) mold release agent and the technique used to apply this agent to glass.

A low-viscosity-grade carboxymethylcellulose powder was dispersed in water at a concentration of 2.5 pph along with 0.12 pph of a medium viscosity grade poly(vinyl alcohol). After the powder was thoroughly dispersed, the mixture was heated to 180°F to effect solution. A nonionic surface-active agent was added to improve the wetting of the glass surface. Only about 0.05 pph of the wetting agent was required. After cooling, the solution was vacuum filtered through No. 1 filter paper on a Buchner filter funnel.

The mold release solution was applied by either of two techniques, flush coating of one surface or dip coating of both surfaces. The plates are allowed to drain in a vertical position for 5 min. at room temperature, then dried at 140°F.

The resulting release film is completely transparent, very smooth, and is about 0.0001 in. thick. The thickness of the film is determined by the viscosity of the solution. The 2.5 pph solution has been found to yield the most consistent release.

III. PREPARATION OF BISBICYCLIC DIEPOXIDES

A. Background and Objective

Water white transparent resins can be made from the diglycidyl ether of bisphenol A (DEBA). However, color at elevated temperatures and thermal stability are not good. Saturated cyclic epoxide resins show superior high-temperature color stability and thermal stability over the (DEBA) epoxy resins.

Typical examples of these resins are 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexanecarboxylate (DDC) and 1-epoxyethyl-3,4-epoxycyclohexane (VCHDO). These compounds produced resins that resisted oxidation and surface discoloration at temperatures 50°F higher than the resins made from DEBA. The heat distortion temperature was improved by 150°F over resins made from DEBA.

The initial color of these resins has not been as good as the initial color of the DEBA resins. However, with the VCHDO resins proper purification of components should give clarity equal to that obtained from DEBA resins. The DDC resin always cured with a light yellow color even when all components were purified to colorless materials. The color in this case is apparently due to chemical properties of the DDC resin and is not caused by impurities.

The objectives of the synthesis work was to prepare monomers which would produce resins with saturated cyclic structures similar to DDC with better thermal stability and freedom from color.

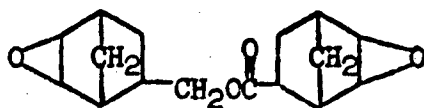## B. Discussion of Results

1. Monomer Synthesis

Synthesis of three diepoxide monomers were attempted.

Bis[2-(bicyclo[2.2.1]heptane-5,6-epoxy)-methyl]carbonate
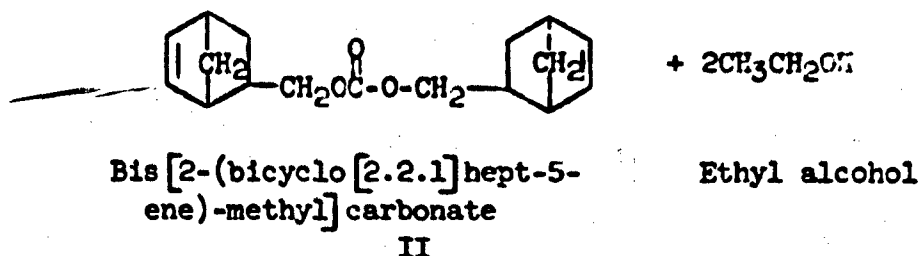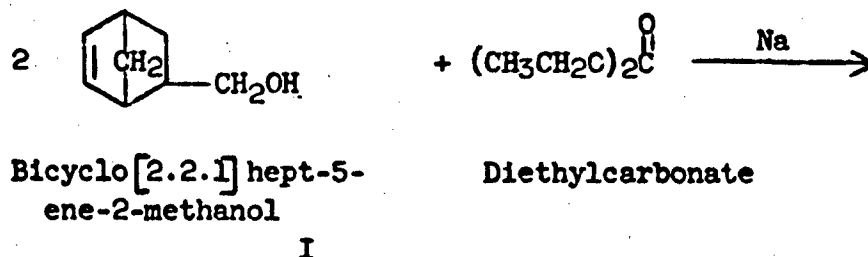

Bis[2-(bicyclo[2.2.1]heptane-5,6-epoxy)-methyl]oxide

5,6-epoxy bicyclo [2.2.1] heptane-2-methyl-5',6'-epoxy-bicyclo-
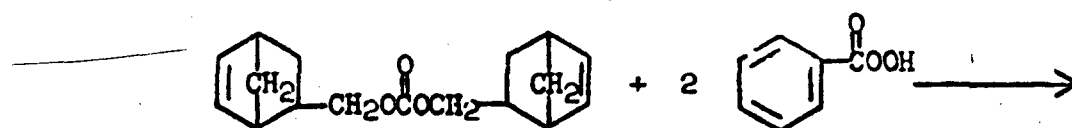   [2.2.1] heptane-2-carboxylate

These diepoxide compounds consist of two bicyclo [2.2.1] heptane rings joined
by different groups. The three connecting groups used were a carbonate, an
ether and an ester.

The endo bridge linkage should add thermal stability to the cyclo-
hexane ring. This principle is demonstrated in the superior thermal rigidity
and stability of resins made with 5-methylbicyclo [2.2.1] hept-5-ene-2,3-dicar-
boxylic anhydride over resins made with phthalic or hexahydrophthalic anhy-
drides.

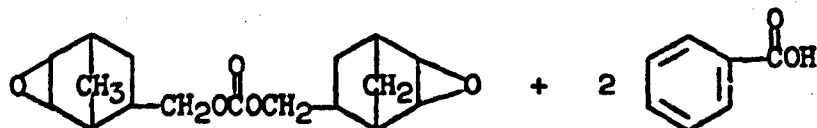The attempted routes of synthesis were as follows:

a. A carbonate linkage:

Bicyclo [2.2.1] hept-5-   Diethylcarbonate
ene-2-methanol
              I

Bis [2-(bicyclo [2.2.1] hept-5-   Ethyl alcohol
ene)-methyl] carbonate
              II

- 50 -

II   +   2 Perbenzoic Acid   ⟶

Bis [2-(bicyclo [2.2.1] heptane-   +   2 Benzoic Acid
5,6-epoxy)-methyl] carbonate
III

Diepoxide III was synthesized and characterized. Initial attempts to epoxidize, using peracetic acid in acetic acid were unsuccessful. Perbenzoic acid in chloroform, ether and benzene was tried. The best results were obtained using perbenzoic acid in benzene. The epoxidation was very slow when ether or chloroform was used as a solvent. All epoxidations were run in the temperature range -4°C to +4°C.

Perbenzoic acid was obtained in excellent yields (85-90 per cent) by very rapid addition of the benzoyl peroxide to sodium methoxide using the quantities specified in Organic Synthesis.[1] A bath of Dry Ice and acetone was used to cool the reaction mixture. Attempts to increase the quantity of perbenzoic acid synthesized in one reaction resulted in reduced yields.
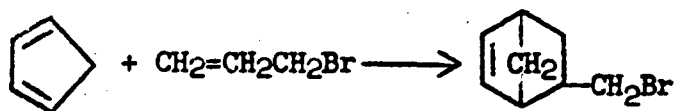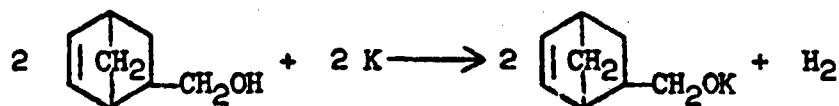
b. **An ether linkage:**
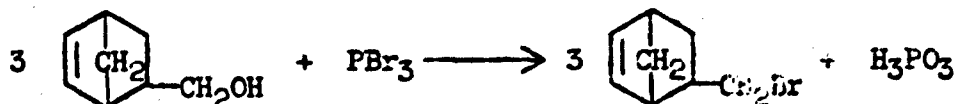
3 I   + PBr$_3$ ⟶ 3 Bicyclo [2.2.1] hept-5-ene-   + H$_3$PO$_3$
2-methyl bromide
IV

---

[1] Gilman and Blatt, "Organic Synthesis", Coll. Vol. I, John Wiley and Sons, p. 431 (1944).

$+ \; CH_2=CH_2CH_2Br \longrightarrow$ [CH_2] $-CH_2Br$

Cyclopentadiene allyl bromide   IV
V

2 [CH_2]$-CH_2OH \; + \; 2 K \longrightarrow 2$ [CH_2]$-CH_2OK \; + \; H_2$

I   Potassium Alkoxide of I
VI

[CH_2]$-CH_2Br \; +$ [CH_2]$-CH_2OK \longrightarrow$ [CH_2]$-CH_2OCH_2-$[CH_2] $+ \; KBr$

IV   VI   Bis [2-(bicyclo [2.2.1] hept-
5-ene)-methyl]oxide
VII

2 $+ \; CH_2=CH_2-CH_2-O-CH_2CH_2=CH_2 \longrightarrow$

V   Allyl Ether

[CH_2]$-CH_2CCH_2-$[CH_2]

VII

$$\text{VII} \quad + \quad 2 \text{ Perbenzoic} \quad \longrightarrow$$

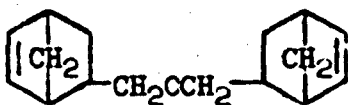$$\text{Bis}\left[2\text{-(bicyclo}\left[2.2.1\right]\text{heptane-5,6-}\right.$$
$$\text{epoxy)-methyl}\left.\right]\text{oxide}$$
$$\text{VIII}$$

$$+ \quad 2$$
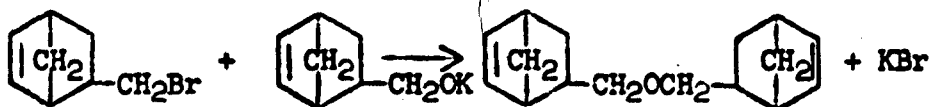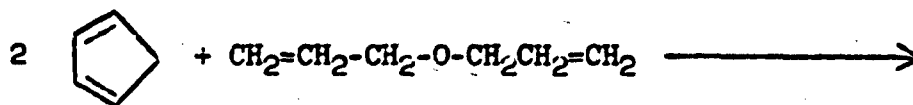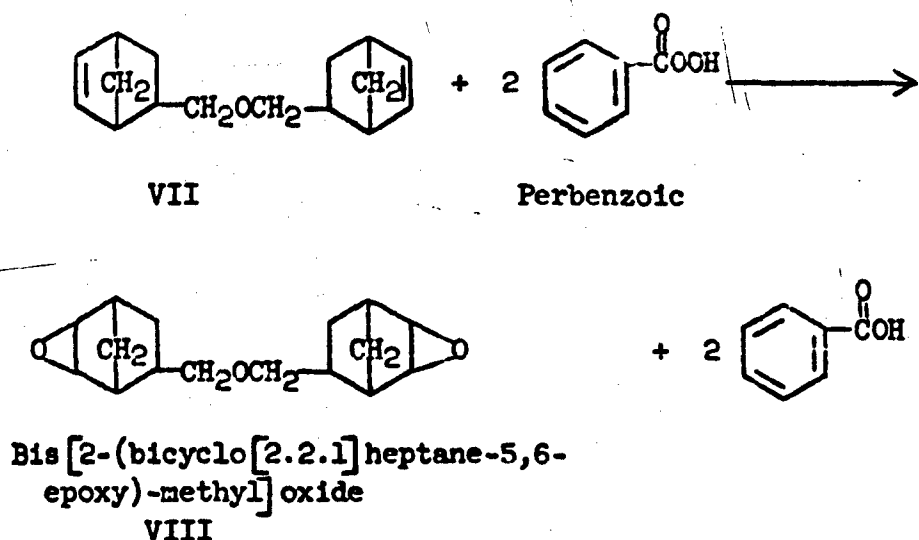
Diepoxide VIII was not synthesized. Synthesis of the intermediate Compound VII was tried by two procedures. The pure compound was not isolated. When diepoxide III was made, it was decided to spend additional time on the curing of this resin. Compound IV was synthesized by two procedures. One procedure involved the replacement of OH of I with bromine. The other was a Diel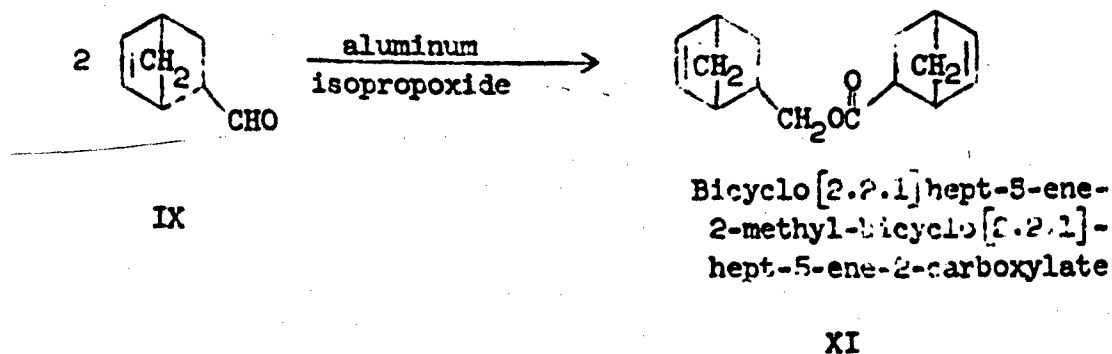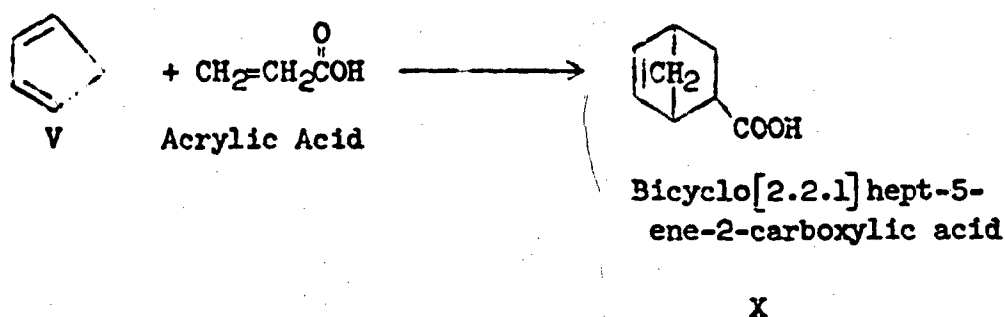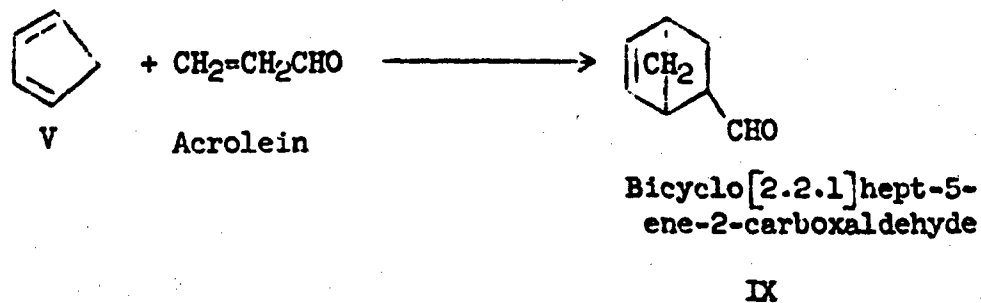s Alder reaction of V and allyl bromide. Three procedures to obtain IV using PBr$_3$ were tried. One run involved the use of pyridine as a moderator. The other runs differed only in the order of addition of reactants. All reactions gave a clear product which distilled at 73-75°C/13 mm). The product obtained was not stable and changed into a yellow mass after standing overnight. Numerous attempts at distillation through various columns failed to prevent the formation of the yellow material. Compound IV was obtained as a stable compound from the reaction of V and allyl bromide. This product had a b.p. of 58-60°C/9 mm.

To obtain a reaction of potassium with I was very difficult. The reaction must be done at temperatures above the melting point of the potassium. The alkoxide readily coats the metal and prevents reaction with the alcohol. After heating for 16 hr. at 98°C, approximately 25 per cent of a stoichiometric amount of potassium was reacted with the alcohol. The reaction of Compounds IV and VI went smoothly. An excess of I was used as a solvent.

Attempts to separate Compound VII by distillation were not successful. Vapor phase chromatography of the last fraction after two distillations showed two components, one of which was Compound I. Measures can be taken to eliminate these difficulties in future work.

Attempts to synthesize Compound VII by the reaction of V with allyl ether have failed. The reaction was carried out in a sealed tube at various temperatures. Temperatures up to 220°C for 16 hr. gave no reaction. Temperatures over 300°C for 16 hr. gave a rubbery material. If Compound VII can be synthesized by this method the temperature would be between 220°C and 300°C.

c. **An ester linkage:**
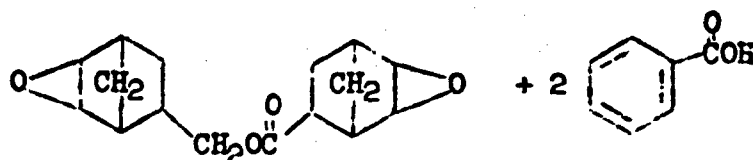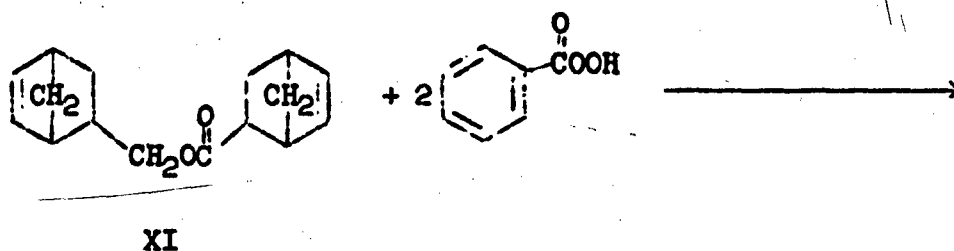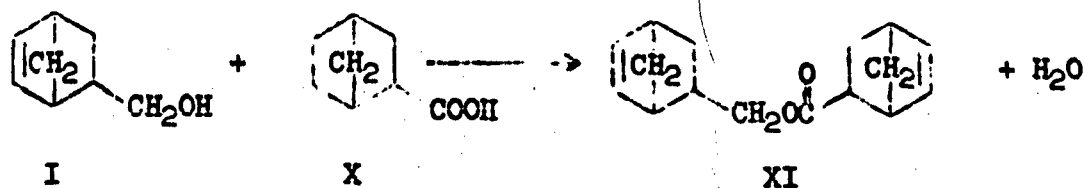
$$V + CH_2=CH_2CHO \longrightarrow IX$$

V   Acrolein

Bicyclo[2.2.1]hept-5-ene-2-carboxaldehyde

IX

$$V + CH_2=CH_2\overset{O}{\overset{\|}{C}}OH \longrightarrow X$$

V   Acrylic Acid

Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid

X

$$2 \; IX \xrightarrow{\text{aluminum isopropoxide}} XI$$

IX

Bicyclo[2.2.1]hept-5-ene-2-methyl-bicyclo[2.2.1]-hept-5-ene-2-carboxylate

XI

- 54 -

I + X $\longrightarrow$ XI + H_2O

XI + 2 COOH $\longrightarrow$

5,6-epoxybicyclo[2.2.1]heptane-2-
methyl-5',6'-epoxybicyclo[2.2.1]
heptane-2-carboxylate
+ 2 COH

XII

Synthesis of diepoxide XII was attempted. Characterization of this compound is not complete. The last fraction of the first distillation analyzed 1 per cent high for carbon. Preparation of the intermediate XI was accomplished by two methods. The Tischenko reaction involving Compound IX gave ca. a 40 per cent yield. The reaction proceeded smoothly without using $AlCl_3$ with the aluminum isopropoxide as the catalyst system. Preparation of XI by condensation of I and X using p-toluene sulfonic acid as the catalyst gave 60 per cent yield at refluxing xylene temperatures. An excess of the alcohol was used. Epoxidation of XI was done by the same procedure as used for diepoxide III.

2. Oxirane Analysis

Functional group analysis of the oxirane ring of several epoxides was tried. The A.O.C.S. Tentative Method cd 9-57 was used to analyze DDC, dicyclopentadiene dioxide, and diepoxide III.

This method involves the use of HBr in glacial acetic acid. The oxirane analysis for DDC was 100 per cent of theoretical, dicyclopentadiene diepoxide consistently analyzed for 65 per cent by this method and diepoxide III consistently analyzed for 60 per cent of theoretical. Other methods were tried without success. Keen[1] gave a procedure for oxetane analysis using refluxing anhydrous pyridine-HCl. With our compounds, this method gave lower results than HBr-glacial acetic acid method. Another method[2] using HIO_4 for vicinal dihydroxy groups gave erratic results. A new method published by Gudzinowicy[3] using dodecanethiol should be tried on the bicyclic type epoxides.

3. Curing of Experimental Resin III

Epoxide resins cure into thermosetting resins with a variety of catalysts. Two main types of cross-linked structures are formed: a polyether formed from a catalyst such as trimethoxyboroxine; and a polyester formed from curing agents such as the anhydrides. Several of the most common types of curing agents were tried with diepoxide III. Figure 43 shows the effect of trimethoxyboroxine on the infrared band of the epoxide group at 850 cm.$^{-1}$. Very little opening of the epoxide ring took place. The resin increased in viscosity after 16 hr. at 140°F. At room temperature the resin was very brittle and upon heating the resin would soften. This indicates that some reaction took place to form a very low molecular weight linear polymer. Figures 44, 45 and 46 show the spectrum of diepoxide III with diethylene triamine, BF_3-monoethylamine and hexhydrophthalic anhydride-benzyldimethylamine curing agents, respectively. These spectra were obtained from samples cast between salt plates which were exposed to the same temperatures as a larger sample of resin. In all of these cases the epoxide band did not decrease appreciably, and a cured resin was not obtained. Maleic anhydride and maleic anhydride with polyol initiators gave hard thermoset resins. Figures 47, 48 and 49 are the spectra for maleic anhydride with trimethylolethane, maleic anhydride with 1,3-propanediol and maleic anhydride. In the system with polyol initiators the epoxide band at 850 cm.$^{-1}$ had nearly disappeared.

---

[1] Keen, R. T., _Analytical Chemistry_, 29, 1041-1044 (1957).
[2] Siggia, "Org. Analysis via Functional Groups", John Wiley (1954).
[3] Gudzinowicy, B. J., _Analytical Chemistry_, 32, 1520-1522 (1960).
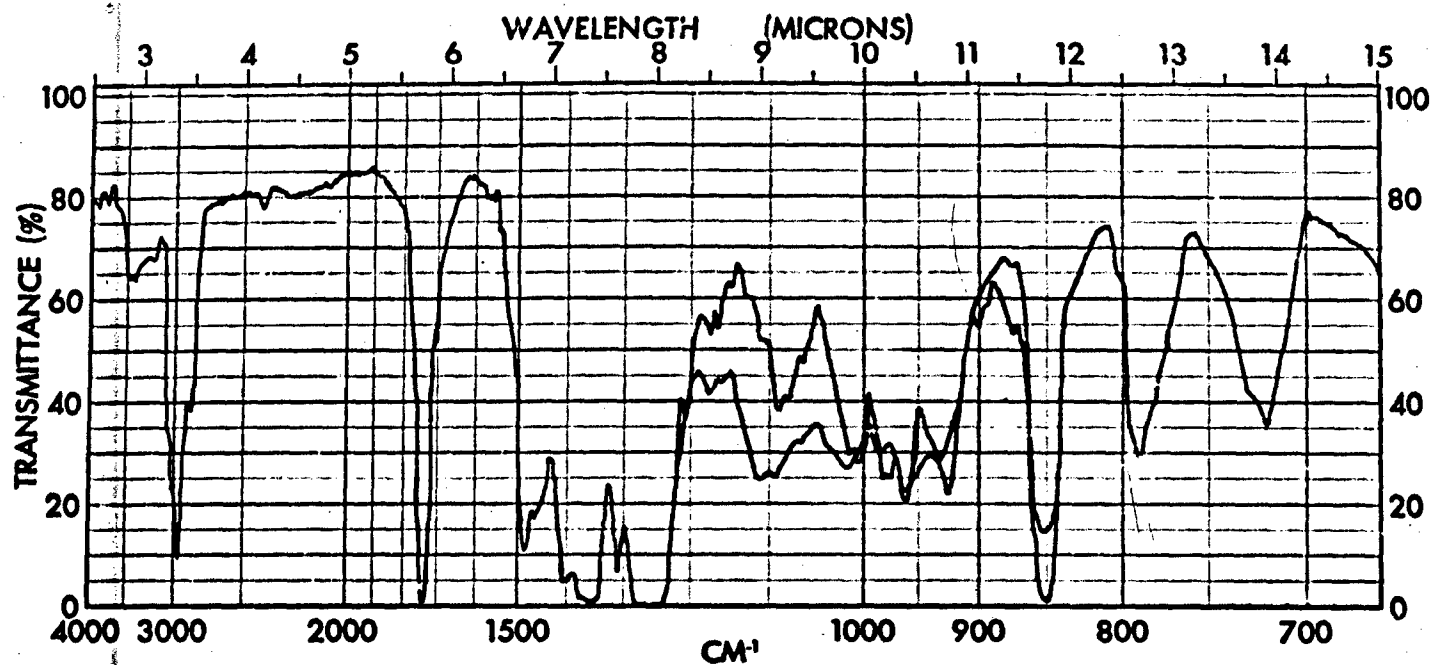
Fig. 43 - Infrared Spectrum of Resin III Cured with TMB
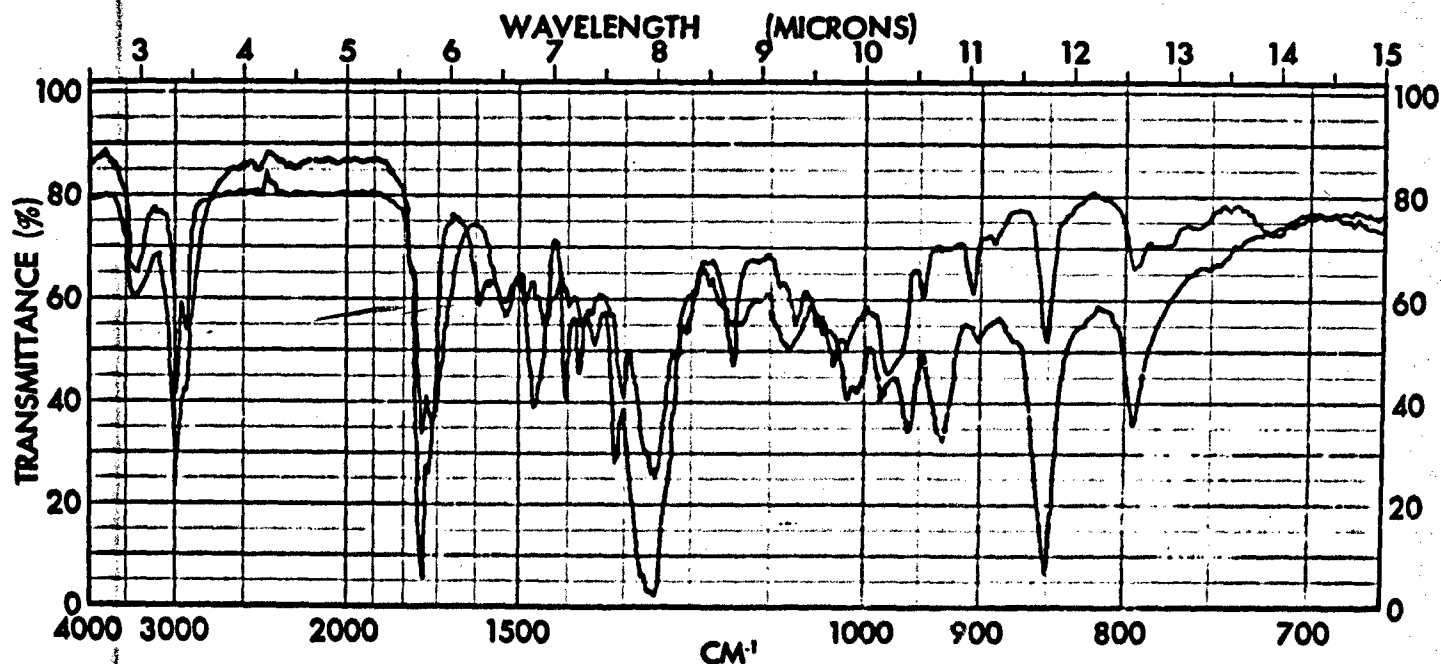

Fig. 44 - Infrared Spectrum of Resin III Cured with
Diethylenetriamine
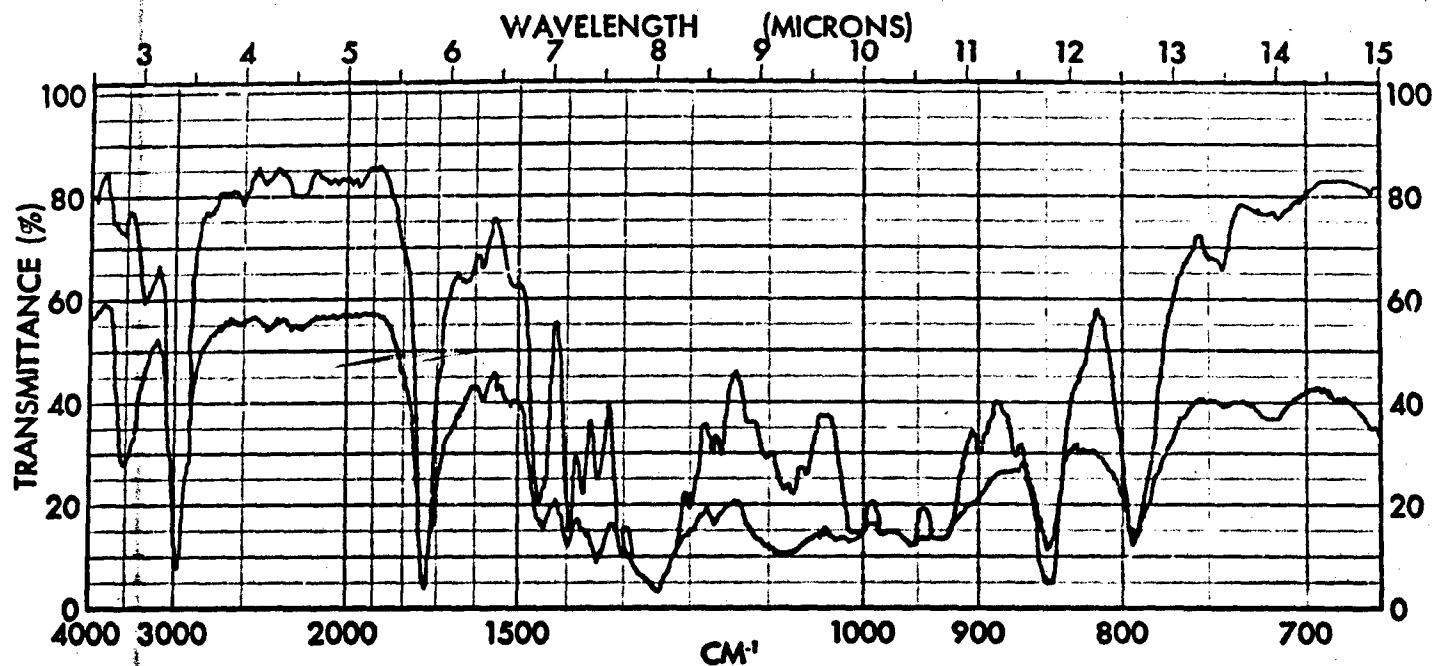
Fig. 45 - Infrared Spectrum of Resin III Cured with
BF$_3$-Monoethylamine
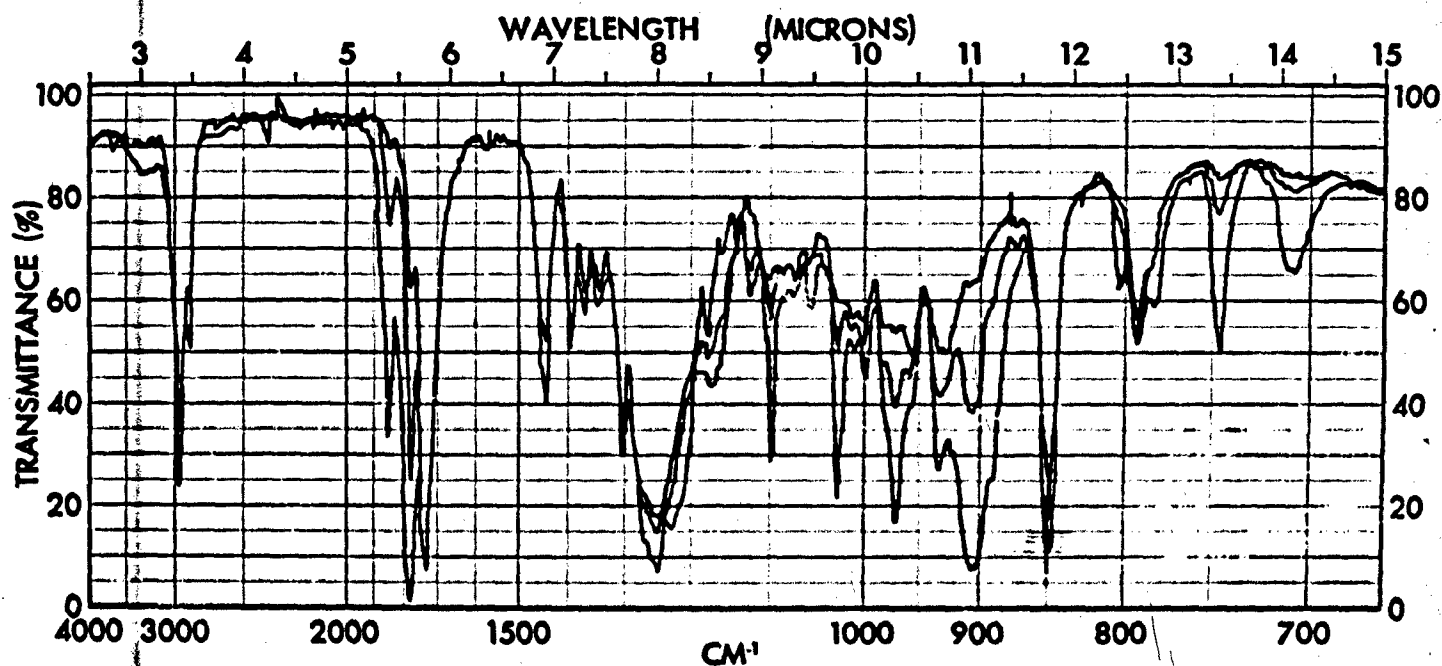

Fig. 46 - Infrared Spectrum of Resin III Cured with
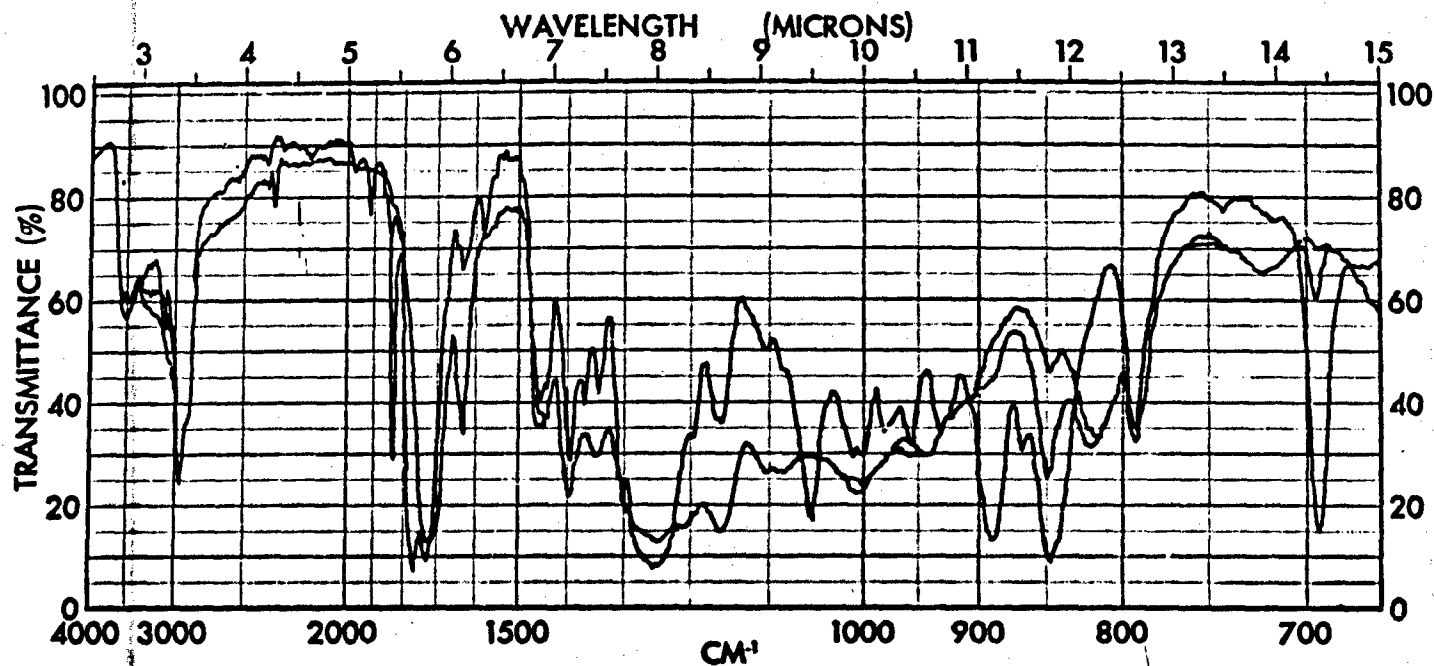HHPA-Benzyldimethylamine

Fig. 47 - Infrared Spectrum of Resin III Cured with Maleic Anhydride
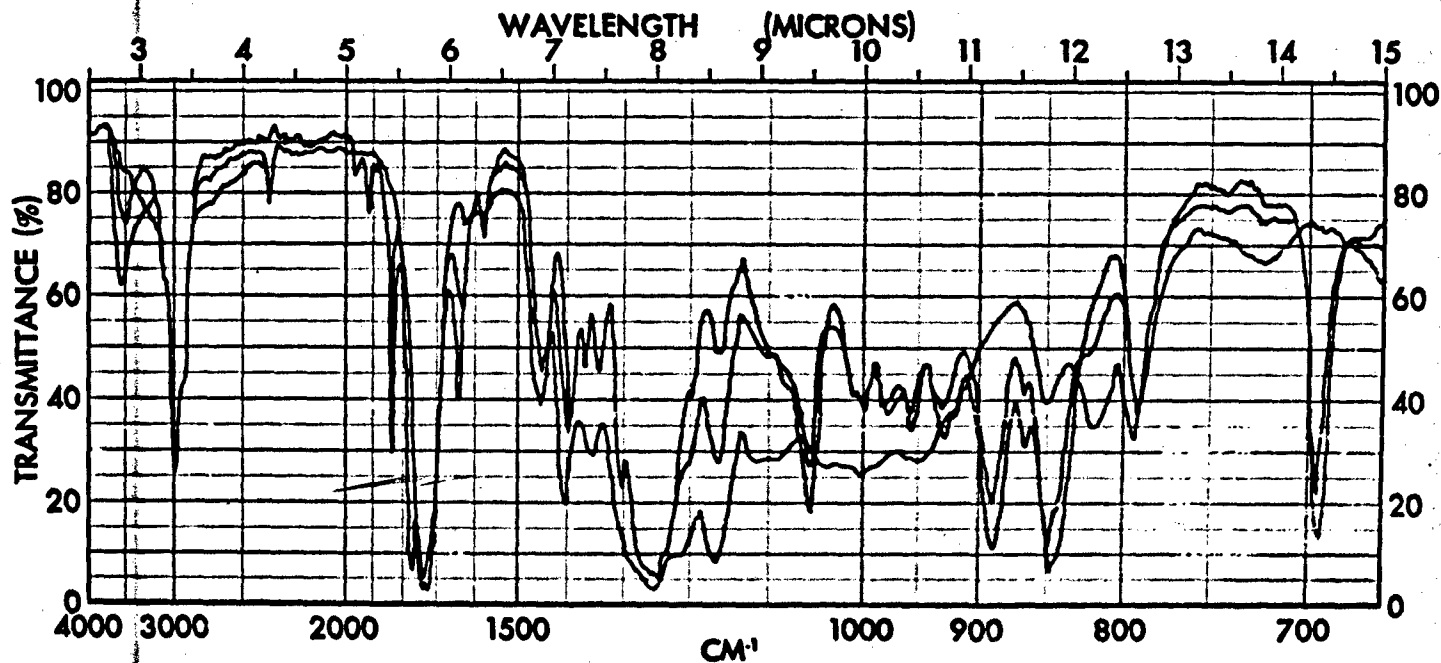and Trimethylolethane

Fig. 48 - Infrared Spectrum of Resin III Cured with Maleic Anhydride
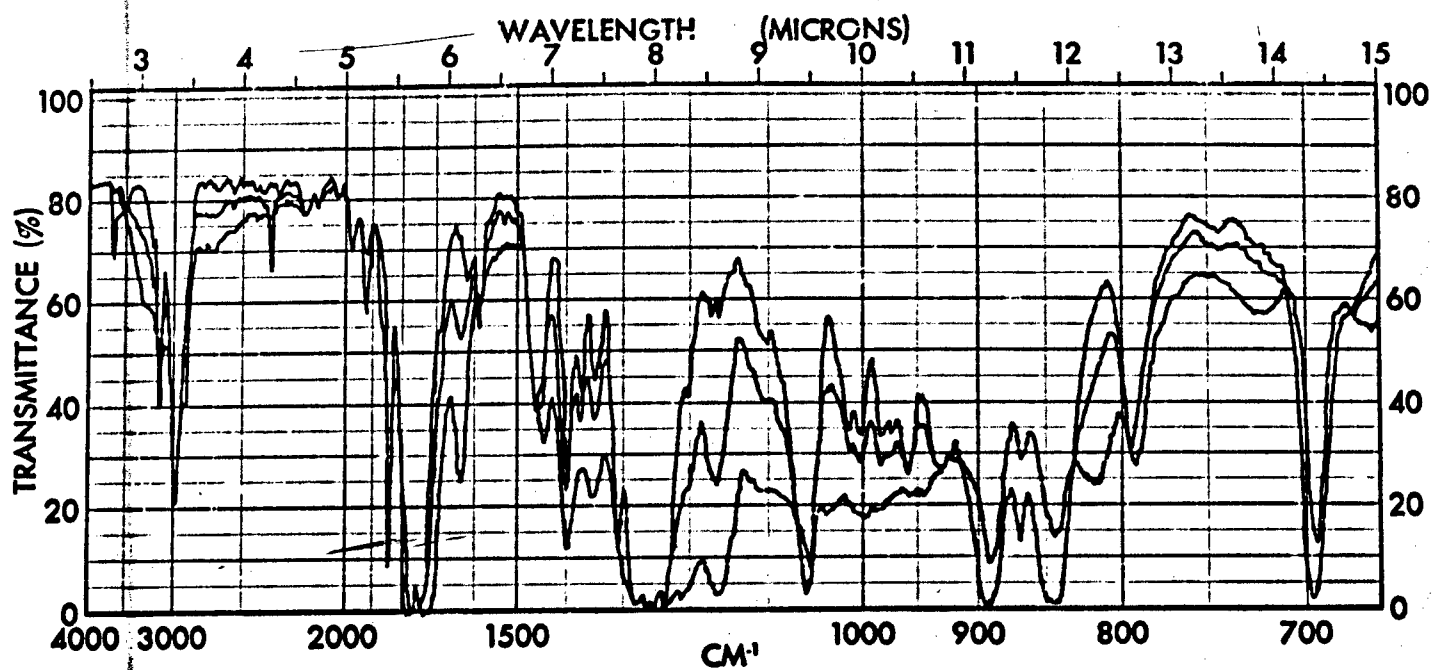and 1,3-Propanediol

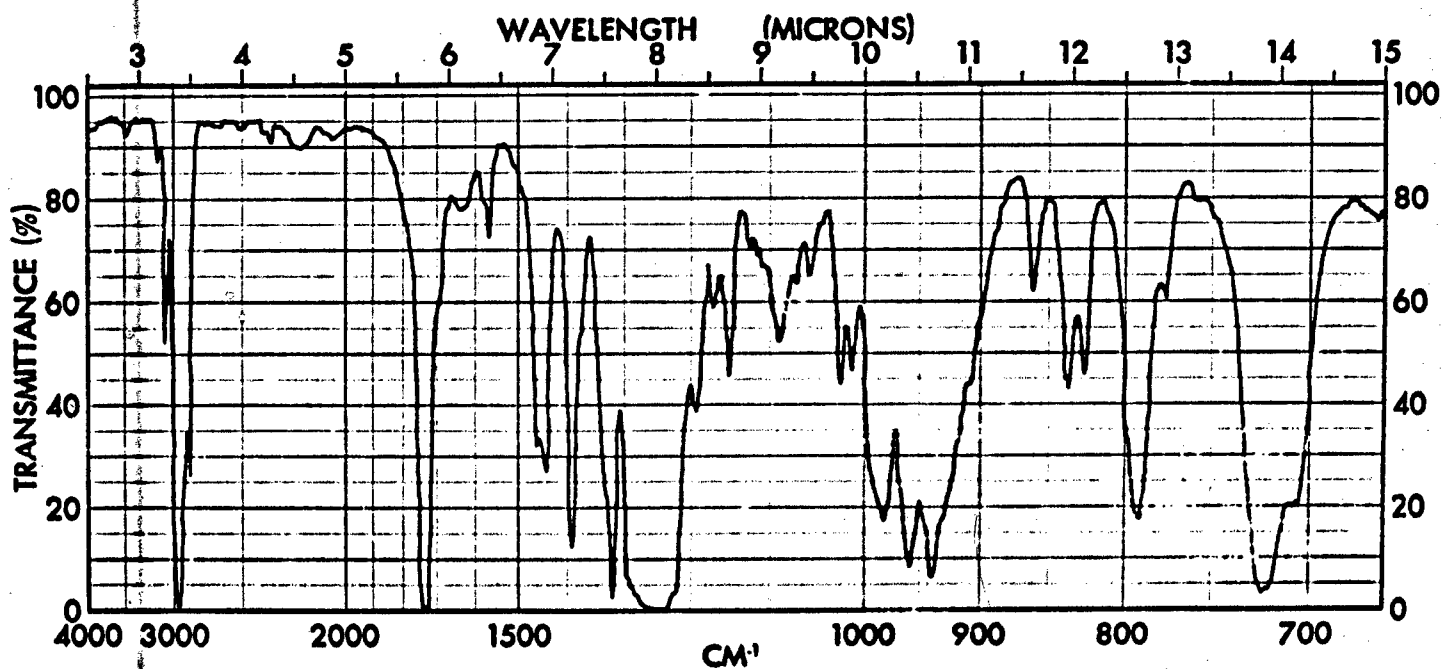**Fig. 49 - Infrared Spectrum of Resin III Cured with Maleic Anhydride**

Fig. 50 - Infrared Spectrum of Compound II

In the system with polyol initiators a thermosetting resin was obtained. The maleic anhydride gave an incompletely cured resin. The reason for the high selectivity in the type of catalyst and conditions for the bicyclic epoxides are not known. This selectivity may also account for the low oxirane analysis. The physical properties of this resin should be evaluated in the future.

C. Experimental

1. Synthesis of Diepoxides and Intermediates

a. Bis[2-(bicyclo[2.2.1]hept-5-ene)-methyl]carbonate   II

Two hundred grams (1.61 mols) of I, 96 g. (0.81 mol) of diethyl carbonate and a small piece of sodium were placed in a 500-ml. three-necked flask. A thermometer, mechanical stirrer and an Oldershaw column were attached to the flask. The mixture was heated. The temperature increased to and held at 155°C; ethyl alcohol was stripped from the mixture as it was formed (R.I., 1.3622 at 25°C, b.p. 78-80°C). A total of 58 ml. of ethyl alcohol was collected which is 62 per cent of theoretical amount. Distillation of the reaction materials gave the product at 140°C/1 mm.

Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.45; H, 8.03.

Found: C, 73.98; H, 7.87.

Iodine No. theo. 185.0. Found: 185.3.

n = 1.5031/24°C infrared spectrum, Fig. 50.

b. Bis[2-(bicyclo[2.2.1]heptane-5,6-epoxy)-methyl]carbonate   III

Perbenzoic acid was prepared from benzoyl peroxide and sodium methoxide in benzene in the usual way.[1]

Forty-five grams (0.331 mol) of perbenzoic acid was added to 45 g. (0.165 mol) of II over a period of 1-1/2 hr. During this period, the reaction mixture was kept between 0 and +4°C. After addition of the perbenzoic acid, the reaction mixture was kept at 3°C until the test for active oxygen was negative. This time was usually about 63 hr. The product was washed with 5 per cent sodium bicarbonate, distilled water and dried

---

[1] Gilman and Blatt, "Organic Synthesis", Coll. Vol. I, John Wiley and Sons, p. 431 (1944).

over sodium sulfate. Distillation at 0.08 mm. gave the following fractions: (1) b.p. 160-170, (2) b.p. 170-172. Eleven grams were collected (22 per cent yield).

Anal. Calcd. for $C_{17}H_{22}O_5$: C, 66.48; H, 7.20.

Found: C, 66.40; H, 7.28.

Oxirane analysis theo. 10.4. Found: 6.3.

n = 1.5108/23°C infrared spectrum, Fig. 51.

c. Bicyclo[2.2.1]hept-5-ene-2-methylbromide   IV

Phosphorus tribromide (0.33 mol) was added to 122 g. (1 mol) of I over a period of 1 hr. in a 500-ml. three-necked flask fitted with thermometer, stirrer and reflux condenser. The temperature was maintained at 25°C. In one run, pyridine was used as a moderator. All reactions gave a product b.p. 73-75°C/13 mm. Reported 75-77°C/13 mm. The product obtained was not stable and overnight changed to a solid yellow mass. The product was reclaimed by redistillation through a column containing 5 perforated plates. A 75 per cent reduction in yield was noted. The product from redistillation also changed into a solid yellow mass upon standing.

d. Bicyclo[2.2.1]hept-5-ene-2-methylbromide   V

Thirteen milliliters of allyl bromide (0.15 mol) and 9.5 ml. of dicyclopentadiene (0.07 mol) were charged into a carius tube, sealed and then heated at 170°C for 8 hr. Distillation yielded a product which had a b.p. 58-60°C/9 mm. Upon standing, no evidence of yellow solid formation was observed. The infrared spectrum was identical to freshly distilled material prepared from PBr_3.

e. Potassium alkoxide of bicyclo[2.2.1]hept-5-ene-2-methanol   VI

One hundred twenty-two grams (1 mol) of I and 39 g. (1 mol) of potassium were heated at 200°F for 6 hr. on a steam bath. The mixture was stirred vigorously. Thirty grams of potassium was recovered. The alkoxide was left in an excess of I which served as the solvent for the etherification.

f. Bis[2-(bicyclo[2.2.1]hept-5-ene)-methyl]oxide   VII

To the molten potassium alkoxide (120°F) of I (0.25 mol) was added a freshly distilled sample of IV (0.25 mol). Excess I was used as the solvent. The reaction mixture was cooled and taken up in ether. The ether
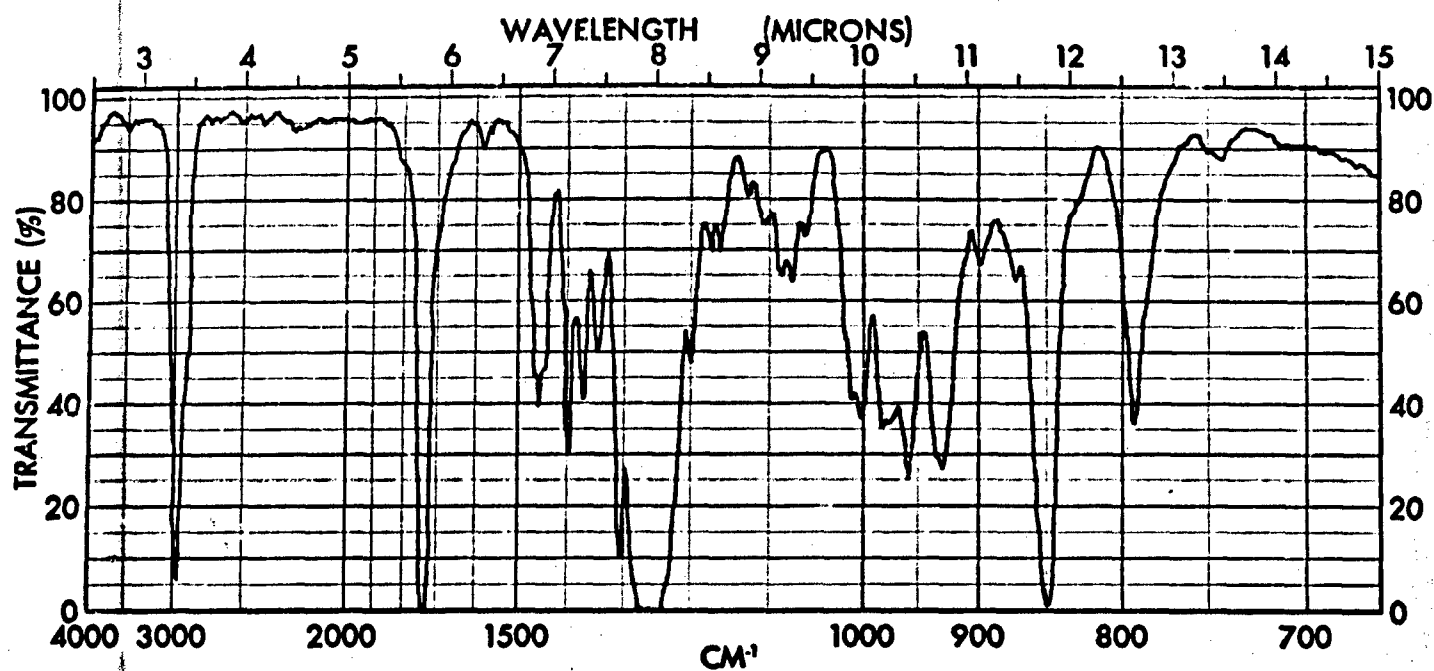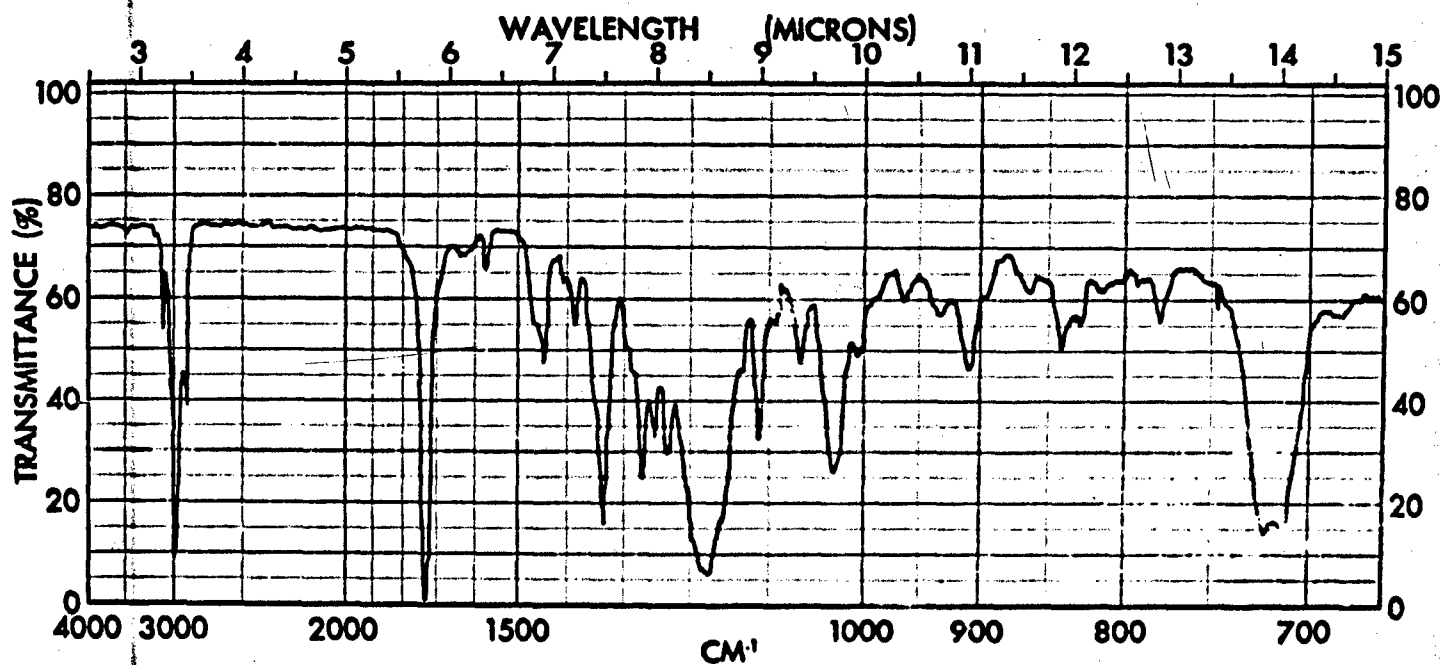
Fig. 51 - Infrared Spectrum of Monomer III

Fig. 52 - Infrared Spectrum of Compound XI

solution was washed several times with water. Distillation of the mixture gave fractions with b.p. 43-50°C/2 mm, n = 1.4979; to 50°C/0.1 mm, n = 1.4990.

Redistillation of the last fractions gave the following fractions: (1) b.p. 29-72°C/4.8 mm, n = 1.4960; (2) 72-75°C/4.8 mm, n = 1.4985; (3) b.p. 75-76°C/4.8 mm, n = 1.4985; (4) b.p. 54-67°C/0.1-0.04 mm, n = 1.5150.

These fractions were gas chromatographed at 250°C. Two fractions were recorded in every case. One of these was the alcohol I.

g. <u>Bis[2-(bicyclo[2.2.1]hept-5-ene)-methyl]oxide</u>   VIII

Dicyclopentadiene (12.3 ml., 0.09 mol) and 11.5 ml. (0.09 mol) of allyl ether were charged into a carius tube. The tube was heated for ca. 15 hr. at constant temperature. Temperatures up to 220°C yielded no reaction products. Temperatures above 300°C gave reaction products that polymerized into a rubbery mass.

h. <u>Bicyclo[2.2.1]hept-5-ene-2-carboxaldehyde</u>   IX

Five-hundred ninety grams (8.95 mols) of cyclopentadiene was added to 500 g. (8.95 mols) of acrolein at room temperature over a period of 4 days. This was limited by the rate of pyrolysis of dicyclopentadiene. The boiling point of the product was 65°C/20 mm, reported 70-72°C/20 mm, n = 1.4852, ρ = 1.0230 g/ml.

i. <u>Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid</u>   X

Four hundred sixty grams (6.95 mols) of cyclopentadiene was added to 500 g. (6.95 mols) of acrylic acid at room temperature over a period of 4 days. The boiling point of the product was 126-130°C/10-12 mm, reported 132-134°C/22 mm.

<u>Anal</u>. Calcd. for $C_8H_{10}O_2$: C, 69.56; H, 7.25.

Found: C, 69.50; H, 7.08.

n = 1.4925/24°C, ρ = 1.130 g/ml at 24°C.

j. Bicyclo[2.2.1]hept-5-ene-2-methyl, bicyclo[2.2.1]hept-5-ene-2-carboxylate   XI

To 42 g. (0.35 mol) of IX in 600 ml. dry ether in a glass stoppered bottle, was added 0.05 per cent by weight aluminum isopropoxide. The reaction was followed to completion by potentiometric titration with sodium sulfite (ca. 8 hr.). Distillation gave a product that had a boiling point of 117°C/0.2 mm.

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.77; H, 8.15.

Found: C, 78.72; H, 8.09.

n = 1.5062/24°C, ρ = 1.0704 g/ml at 24°C.

Infrared spectrum, Fig. 52.

k. Bicyclo[2.2.1]hept-5-ene-2-methyl, bicyclo[2.2.1]hept-5-ene-2-carboxylate   XI

In a 5-liter, three-necked flask, fitted with thermometer and reflux condenser and Dean Stark tube was added 610 g (4.43 mols) of X, 650 g. (5.25 mols) (100 g. excess) of I, and 2.5 per cent by weight (based on weight of X) of p-toluene sulfonic acid and 1,500 ml. xylene. The mixture was refluxed at 152°C until water was no longer eliminated. Seventy per cent of the theoretical amount of water was obtained. The mixture was washed with 5 per cent $NaHCO_3$ and distilled water. Distillation gave a product with boiling point 120°C/0.2 mm. This product was identical to that obtained by Tischenko reaction of compound IX.

l. 5,6-epoxybicyclo[2.2.1]heptane-2-methyl-5',6'-epoxybicyclo [2.2.1]heptane-2-carboxylate   XII

The same epoxidation procedure was used as described for preparation of III. Distillation gave the following fractions: (1) b.p. 112-130°C/0.065 mm (ca. 2 g.), (2) 135-136°C/0.07 mm (ca. 2 g.). Eighty per cent of the material remained in the distillation flask as a tar.

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 69.56; H, 7.24.

Found in Fraction (2): C, 70.73; H, 7.25.
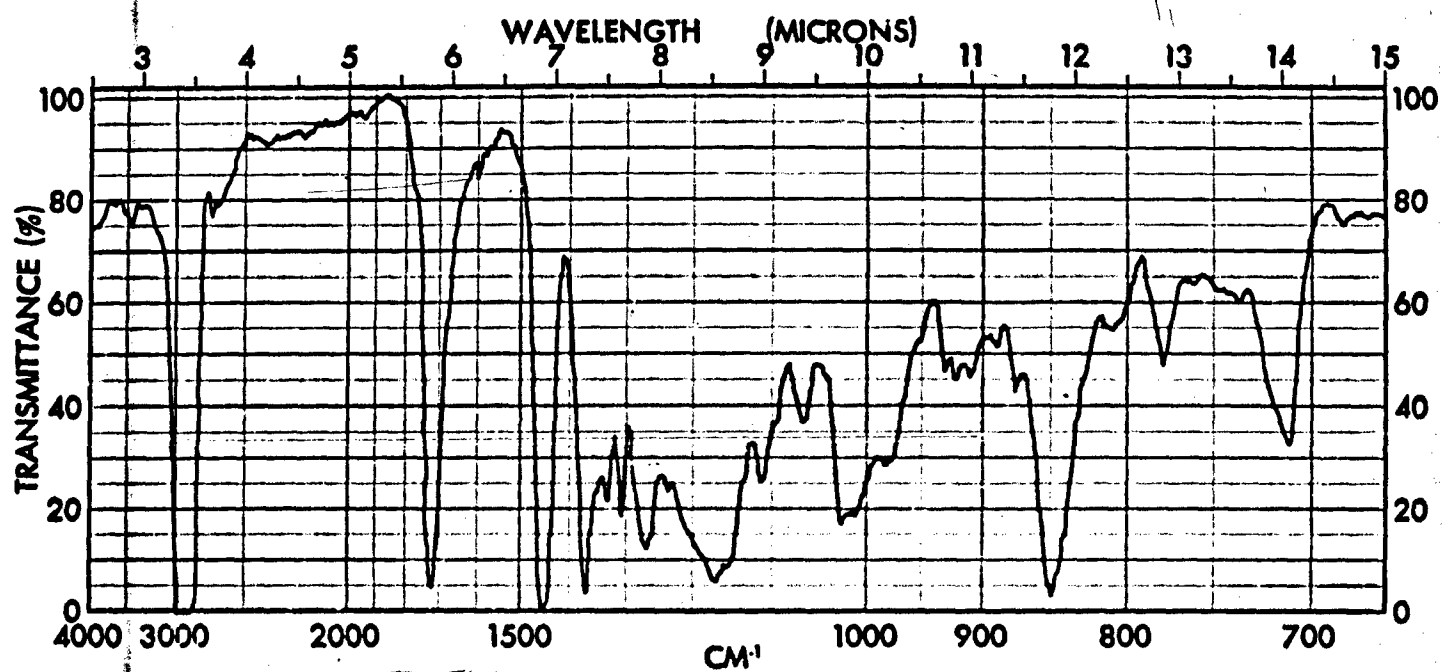
Infrared spectrum is shown in Fig. 53.

Fig. 53 - Infrared Spectrum of Monomer XII

2. Oxirane Analysis

Three procedures have been tried for the analysis of the epoxide functional group. The procedure, resin, and results are listed in the tables below.

TABLE VIII

A.O.C.S. TENTATIVE METHOD CD 9-57 (HBr-ACETIC ACID)

Resin		Modification of Procedure	Results (%) of Theory
DDC		None	100
Dicyclopentadiene Dioxide		None	65.9
"	"	2 hr. standing time	66.4
"	"	3 hr. " "	65.9
"	"	4 hr. " "	65.9
"	"	5 hr. " "	67.0
"	"	16 hr. " "	65.3
Resin III		None	57.0
" "		"	61.0

TABLE IX

REFLUXING PYRIDINE HC1[1]/

Resin		Modification of Procedure	Results (%)
Dicyclopentadiene Dioxide		Reflux 1 day	34.0
Resin III		Reflux 3 hr.	34.0
" "		Reflux 4 hr.	33.6
" "		Reflux 5 hr.	41.4
" "		Reflux 6 hr.	24.0

---

[1]/ Keen, R. T., Analytical Chemistry, 29, 1041-1044 (1957).

TABLE X

PERIODIC ACID[1]

Resin		Modification of Procedure				Results (%)
Dicyclopentadiene Dioxide		1 day standing time				30.8
"	"	3 days	"	"		64.7
"	"	3	"	"	"	64.9
"	"	6	"	"	"	80.9
"	"	6	"	"	"	121.5
"	"	8	"	"	"	89.1
"	"	8	"	at 100°F		105.8
"	"	10	"	"	"	128.5

[1] Siggia, "Org. Analysis via Functional Groups", John Wiley, 1954.

3. Curing of Experimental Resin III

Figures 43 through 49 show the spectrum of Resin III with various curing agents. Approximately 15 g. of Resin III was used. To reduce the viscosity, the resin was warmed to ca. 140°F before mixing. Immediately after mixing, one drop of the resin and catalyst mixture was cast between salt plates and the spectrum run immediately. The spectrum was taken at various intervals during the cure cycle. Attention was focused on the epoxide band at 850 cm.$^{-1}$. Generally two spectra of each catalyst system are shown, the first spectrum after mixing, which has the greatest absorbance at 850 cm.$^{-1}$, and the spectrum obtained after considerable cure time. Figures 46 through 49 have a spectrum taken approximately 2-4 hr. after being at temperature. The absorbance of the band at 850 cm.$^{-1}$ in these cases lies between the absorbance of the first and last spectra.

Table XI lists the various curing agents, time and temperature of cure.

TABLE XI

RESIN III WITH VARIOUS CURING AGENTS

Figure	Curing Agent	Concentration of Curing Agent	Time	Temperature (°F)	Results
43	TMB	5 pph	1 week	140-180	Increase in viscosity
44	Diethylenetriamine	10 pph	1 week	180	No increase in viscosity
45	BF$_3$-monoethylamine	2.5 pph	1 week	180-250	Increase in viscosity
46	HHPA-benzyldimethylamine	0.8 mol/mol epoxy	1 week	180	Increase in viscosity
47	Maleic anhydride-trimethylolethane	3.0 mol/3.0 mol epoxy/0.7 mol TME	24 hr.	180	Cured resin
48	Maleic anhydride-1,3-propanediol	3.0 mol/3.0 mol epoxy/0.7 mol 1,3-diol	24 hr.	180	Cured resin
49	Maleic anhydride	stoichiometric	1 week	180	Incompletely cured resin